THERMODYNAMIC INDICES OF TARTARIC CRYSTALLIZATION DURING THE STABILIZATION OF YOUNG WHITE WINES

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Abstract: Clarity is an essential quality required by consumers, especially for white wines in clear glass bottles. The present work was undertaken to study the effect of the industrial stabilization process on the potassium bitartrate stability and composition of white wines. Under laboratory conditions of refrigeration were tested and monitored before and after the refrigeration test. According to achieved results was observed a decrease of stabilization time by 4-6 days, the thermodynamic concentration product (PCT) of potassium ions and bitartrate had diminished in proportion of 20,8÷28,07 %. In terms of organoleptics, the treatment of wines enhances the aroma expression, the flavor persistence and specific color for this type of wine.

Key words: young white wine, crystalline stabilization, refrigeration, thermodynamic indices

Introduction

The days when wineries can release wines to the public with physical instabilities and still compete has long past. It is essential that every vintner understand the parameters affecting wine stabilities and operate to obtain product stability while maximizing palatability. In winemaking it is usually necessary to reduce the concentration of potassium bitartrate (KHT) in wine to avoid its precipitation in the bottle, which otherwise could reduce perceived wine quality. All wines differ in their „*holding*" or retention capacity for tartrate salts in solution. If the holding capacity is exceeded, these salts will precipitate, resulting in the formation of „*tartrate casse*". Solubility of potassium bitartrate is dependent primarily upon the alcohol content, pH, the temperature of the wine, and the interactive effects of various cations and anions [1].

The conventional process for tartaric stabilization of young wines consists of cooling the wines at a temperature near the freezing point for several days to induce KHT precipitation before bottling [2]. This process is carried out in two procedures: conventional cold stabilization (chill-proofing) and contact seeding (addition crystals of potassium bitartrate). Thus, the addition of these crystals to wine causes it to become super-saturated with respect to potassium bitartrate and this is precipitated rapidly from solution [3] and [4].

The present study was conducted in order to study the stabilization of young white wines and the evolution of thermodynamic stability indices. The study of the influence of stability procedures (above named) on the solubility and the forms of potassium bitatrate from wines, allowed us to obtain data necessary for explaining physico-chemical phenomena, which influence stability or instability during wine stabilization treatments, related to the precipitation of tartaric salts.

Materials and Methods

Investigations have been conducted on a white wine obtained from *Chardonnay* variety of vintage 2013. Experiments were carried out during september-december 2013, at the Oenology Research Centre of Technical University of Moldova and at the National Audit Centre of Alcoholic Products, Chisinau, republic of Moldova.

Physico-chemical analyses of the wine were carried out on the alcohol content, total acidity, pH, content of tartaric acid, potassium and others, using the methods presented in national and international standards [5] - [6]or literature and are shown in Table 1.

Initially, the wine samples have been fined with bentonite in order to ensure the protein stability, and then tartaric stabilized by two methods: conventional cold stabilization and contact seeding with 5 g/l KHT at the temperature of minus 5°C. After the stabilization by two procedures, the wine samples were filtrated at the seeding temperature to avoid resolubilization of potassium bitartrate crystals back into wine.

The cations present in the wines before and after the tartaric stabilization were determined by a OIV recommended method using atomic absorption spectrometry. The content of organic acids was determined by capillary electrophoresis.

The tartaric stability is a relative term that can be and is checked by different tests. Two traditional methods of determining potassium bitartrate stability were applied: the determination of CP's (Concentration Product values) and the „*conductivity*" test. The relationship between tartaric acid and potassium ions is expressed quantitatively by using the CP and measuring the electrical conductivity change in a KHT-seeded wine by the disappearance of free potassium ions (K^+) from solution. If this difference is less than 5% of the initial value, the original wine is considered to be stable, if not the wine is unstable and can be retreated. The change of electrical potential (conductivity) was measured with a standard conductivity meter, using a conductivity cell with a constant of 1 cm^{-1}.

Data obtained after determining the content of potassium, alcohol, total tartaric acid and pH values were used for the calculation of wine ionic power (μ) and activity coefficients (γ_1, γ_2), for monovalent (K^+, HT^-) and bivalent ions (T^2) according to the methodology proposed by [7]. According to them it was calculated the product concentration (PC) and the product of thermodynamic product (PCT) of potassium bitartrate (Tratatul lui Cotea). The thermodynamic solubility product (PST) of potassium bitartrate in hydroalcoholic solutions saturated with KHT (at the ionic power of the studied sample) at the temperature of −4 ºC, and the solubility product (PS) at wine ionic power at −4ºC were calculated according to data from literature sources [8].

Results and Discussion

The data concerning the main wine composition characteristics before and after the stabilization are presented in table 1. According to these data, the wine samples during the stabilization diminished the color intensity, the content of tartaric acid and total polyphenol index within the limits of 23÷40 % of the initial values. Also, the content of tartaric acid and potassium in samples has decreased in the following order: 9,87 % and 23,8 % (for sample 1) and subsequently 22,42 % and 26,4 % (for sample 2).

Table 1. Physico-chemical characterization of the white wines.

№	Parameter	Wine sample					
		Sample 1 of wine			Sample 2 of wine		
		Initially	Stabilized by chill-proofing	Stabilized by contact seeding	Initially	Stabilized by chill-proofing	Stabilized by contact seeding
1	Ethanol (%v/v)	12,62	12,48		12,42	12,22	
2	pH	3,13	3,08	3,06	3,27	3,13	3,11
3	Total acidity, g/l $C_4H_6O_6$	7,82	6,80	6,72	7,94	6,90	6,86
4	Volatile acidity, g/l CH_3COOH	0,42	0,48		0,45	0,53	
5	Content of tartaric acid, g/l	1,76	1,62	1,58	1,85	1,46	1,41
6	Content of potassium, g/l	0,920	0,713	0,682	0,846	0,643	0,613
7	Color intensity, $A_{420\ nm}$	0,092	0,048	0,042	0,089	0,054	0,052
8	Total polyphenol index (TPI) mg/l	148,76	86,31	82,54	132,49	88,12	86,38
9	Conductivity at 20°C, μS/cm	1988	1670	1620	1813	1510	1530
10	Organoleptic analysis, points	7,7	7,8		7,9	8,0	8,1

From the comparative analysis of the two procedures is revealed that the decrease of all parameters is more significant in the case of contact seeding procedure in comparison with conventional cold stabilization. The conductivity has diminished in average with 15,9 % and the total polyphenol index with 40 %. In terms of organoleptic analysis, the treatment of young wines enhances the aroma expression, the flavor persistence and specific color for this type of wine.

According to data presented in Table 1 were calculated in wine the ionic power (μ) and the activity coefficients (γ_1, γ_2), for monovalent (K^+, HT^-) and bivalent ions (T^2) showed in table 2 and with its evolution.

Table 2. Thermodynamic indices of tartaric crystallization of samples.

№	Parameter	Wine sample					
		Sample 1 of wine			Sample 2 of wine		
		Initially	Stabilized by chill-proofing	Stabilized by contact seeding	Initially	Stabilized by chill-proofing	Stabilized by contact seeding
1	Theoretical saturation temperature, ºC	18,6	10,8	10,2	18,9	10,43	10,06
2	Content of ion bitartrate, 10^{-3} mol/L	6,2	5,45	5,07	6,25	5,71	5,57
3	Concentration product (PC), 10^{-6} mol^2/L^2	146,0	93,9	86,7	141,1	93,9	87,3
4	Solubility product (PS) at minus 4°C, 10^{-6} mol^2/L^2	21,16	20,45	20,31	22,01	21,54	21,48
5	Solubility product (PS) at 20°C, 10^{-6} mol^2/L^2	158,31	153,01	151,91	164,90	161,34	160,95
6	Ratio PC/PS at minus 4°C	6,89	4,59	3,81	6,41	4,36	4,06
7	Ratio PC/PS at 20°C	0,873	0,538	0,518	0,786	0,586	0,518

In wine samples the concentration product is ranging between 141,1 and 146,0·10^{-6} mol^2/L^2, and it is 7 time higher than the solubility product at minus 4°C. Therefore, being in a risk area, it may be out of the metastable equilibrium resulting in the precipitation of THK in these wines even at the temperature of 15°C.

The values of solubility product at wine ionic power was estimated according to thermodynamic solubility product of KHT, which values were 14,09 and 14,80·10^{-6} mol^2/L^2, respectively. After stabilization, the wine content of ion bitartrate decreased with 1·10^{-3} mol/L and the diminished concentration product is ranging between 47,2 and 59,3·10^{-6} mol^2/L^2.

Final calculation of the thermodynamic indices of tartaric stability has described a correlation between PC and PS of 4 to 1, so the speed of formation and growth of crystals KHT are inhibited due to remaining colloidal compounds in wines. The samples of wine are not prone to tartaric precipitation although PC is 3-4 times higher than PS.

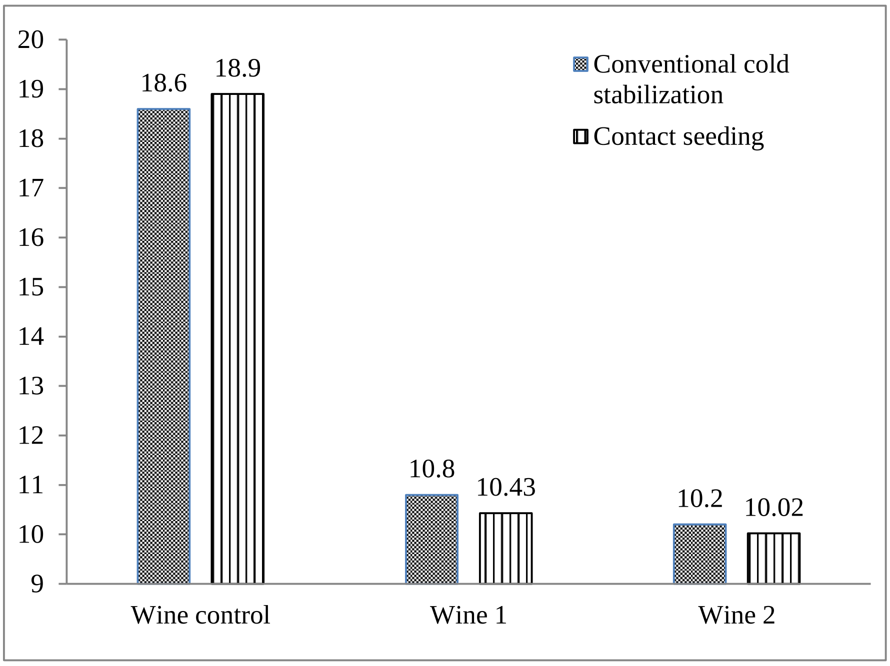

Fig. 1. The evolution of the saturation temperature depending on the process applied.

Theoretical saturation temperature (T_{sat}) of potassium bitartrate has decreased from 18 to 10°C in wines during the stabilization and much more significant at contact seeding procedure in comparison with conventional cold stabilization by the complexion or "*fouling*", factors that affect formation and growth of the potassium bitartrate crystals are taken into account.

Conclusion

These results show that the CP's criteria give results compatibles with the „*conductivity*" test for the white wines. As a result of tartaric stabilization, total acidity had an increased value, of almost 21%, and pH has decreased in the following order: 1,6 % (sample 1, in the case of conventional cold stabilization) and 4,9 % (sample 2, in the case of contact seeding). The cold stabilization of wines in all the cases, the values of constants characterizing solubility were relatively diminished. The content of bitartrat ion decreased with $1 \cdot 10^{-3}$ mol/L, the diminished of concentration product is ranging between 47,2 and $59{,}3 \cdot 10^{-6}$ mol^2/L^2 and the theoretical saturation temperature of KHT decreased from 18,60 to 10,4 °C in sample wines.

Relying on comparative analysis of the two procedures, we recommend the contact seeding procedure for stabilization of the young white wines for economic and technological reasons.

This study of stabilization methods allowed us to obtain data necessary for explaining physico-chemical phenomena, which influence stability or instability during young white wines stabilization treatments related to the precipitation of tartaric salts.

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