ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2015, *60*(11-12), 1019-1024

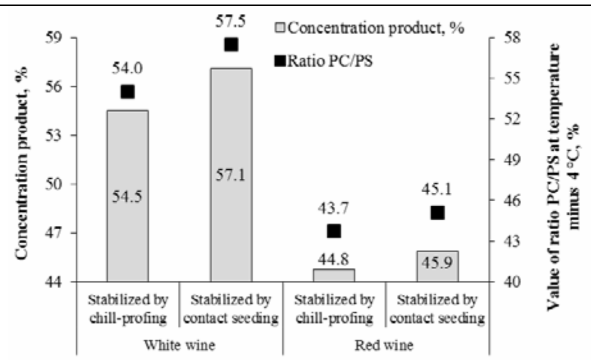
TARTARIC STABILIZATION OF YOUNG WINES AND THERMODYNAMIC INDICES OF STABILITY**

Rodica STURZA[a] and Ecaterina COVACI [b,*]

[a]Technical University of Moldova, 168 Stefan cel Mare str. , Chisinau, MD-2004, the Republic of Moldova
[b]Institute of Chemistry, Academy of Sciences of Moldova, 3 Academiei str., Chisinau MD-2028, the Republic of Moldova

Received July 25, 2014

The excess of tartaric salts determines in certain conditions the formation of characteristic crystals that fall in the sediment form. The aim of this study is to obtain thermodynamic indices during cold stabilization of young wine samples (*Chardonnay* and *Pinot Noir* variety). According to the achieved results, cold stabilization reduces the values of concentration product of samples in the limits of 44.77÷57.10 % of initial values. The optimal regime for tartaric stabilization of young wines has been established in economic and technological reasons.



INTRODUCTION

Clarity is one of the leading consumer quality requirements. It is an important aspect of a consumer's first contact with a wine and a key element in visual satisfaction. Turbidity is undeniably a major negative factor in assessing a wine.[1] The most important variables affecting the precipitation of potassium bitartrate (KHT) are: the alcohol content, the pH, the temperature of wine storage and the interaction of various cations and anions effects.[2] The techniques currently used in the processing wine units to prevent KHT precipitation in wines include: cations exchange,[3] electro dialysis and refrigeration.[4] In young wines KHT is always present in oversaturating concentration and crystallizes spontaneously, so the refrigeration is the only recommended method for this category of wines. This process consists in cooling the wine at a temperature near the freezing point for several days (physical treatment) to induce KHT precipitation before bottling.[5] This process is called cold stabilization and is carried out in two procedures: conventional cold stabilization (chill-proofing) and contact seeding (addition of potassium bitartrate crystals). The KHT crystals additions in wine generate the oversaturation state at negative temperature of stabilization and rapidly precipitate in wine.[6]

The present study was conducted in order to study the effect of the industrial stabilization process on the potassium bitartrate stability and to estimate the evolution of thermodynamic indices of young wines. In the laboratory conditions were

** Paper presented at COFrRoCA 2014: Huitième Colloque Franco-Roumain de Chimie Appliquée, 15 – 18 Septembre 2014, Montpellier, France.
* Coresponding autor: covaci_ecaterina@yahoo.com

tested two stabilization process and physico-chemical parameters of wine samples before and after the stabilization are evaluated and discussed.

MATERIALS AND METHODS

Investigations have been conducted on two young wine of *Chardonnay* and *Pinot Noir* variety of vintage 2013. Experiments were carried out during September-December 2013, at the Oenology Research Centre of Technical University of Moldova and the National Audit Centre of Alcoholic Products, Chisinau, the Republic of Moldova. The wine samples submitted for studio were obtained by classic technological schemes and the physico-chemical parameters were carried out on the: alcohol content, the total acidity, the pH value, the content of tartaric acid, potassium and others, using the presented in national[7] and international standards methods.[8] The contents of cations in wines before and after the tartaric stabilization were determined by the recommended International Organization of Vine and Wine (IOVV) method, using atomic absorption spectrometry[9] and the content of organic acids by capillary electrophoresis.[10] Data obtained were used to calculate the ionic strength (μ), the activity coefficients (γ_1, γ_2) for monovalent (K^+, HT^-) and bivalent ions (T^2) according to the proposed methodology.[11] The concentration product (PC), thermodynamic product (PCT) and thermodynamic solubility product (PST) of KHT were calculated according to literature sources.[12]

Initially, the white wine samples have been fined with bentonite of Solub type[13] at doses 0.75 g/L and those red with gelatin of Pulviclar S type[14] at 0.35 g/L, in order to ensure the colloidal stability. The dose of gluing agent for wine samples has been determined by the preliminary test, filtered and tartaric stabilized by two methods: conventional cold stabilization and static contact seeding with 5 g/L KHT at the temperature of minus 5°C.[15] After the stabilization by the above-mentioned methods, the wine samples were filtrated at the seeding temperature, to prevent the resolubilization of potassium bitartrate crystals into wine.[1] During the stabilization the samples have been tested at tartaric stability by a conventional process consisting in cooling the wines at a temperature of minus 5°C for 2 days with the preliminary administration of KHT oversaturated solution and intensive homogenization to induce the KHT precipitation. At the end of period, the samples are visual inspected and conclude on the presence or the absence of KHT crystals. The test results, therefore, indicate the final stability of wine and it presents a risk of tartrate precipitation. The sample of wine was considered to be stable, if the tartaric crystals are missing, if not the wine is unstable and will be cold retreated.[16] The most appropriate experimental schema of wine cold treatment is presented in Fig. 1.

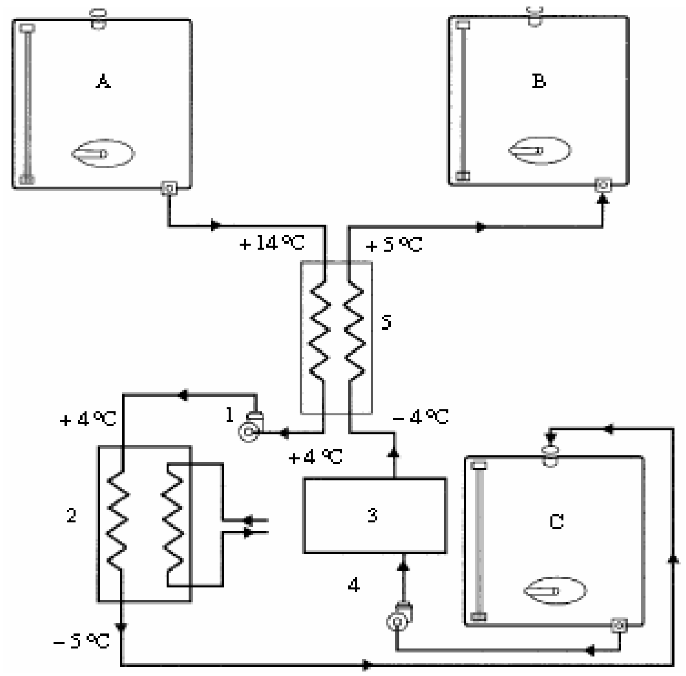


Fig. 1 – Schema of cold stabilization installation, where A: untreated wine (+14°C), B treated wine (+5°C) and C wine during stabilization (−5°C).

The sensory analysis on each considered wine was carried out separately with a panel of 16 trained judges using the triangle test and the global preference.[17] All measurements were carried out in triplicate and the results were statistically analyzed using the Statistica 6.0 program to determine the average value and standard error. With the aim of elucidation the optimal conditions for tartaric wine stabilization was established the empirical model in form of binomial regression equation ($n = 2$ and $p \leq 0.005$) and its 3D interpretation was made using Gruplot 5.0 selecting the variation range of each selected factor.[18]

RESULTS AND DISCUSSION

The data concerning the main wine composition characteristics before and after the tartaric stabilization are presented in Table 1, where the parameters as color intensity, content of tartaric acid and total polyphenol index diminished in the limits 23÷40% of the initial values. The technique of refrigeration microbiologically purifies the new wines, stabilizing the color and the flavor, particularly red wines bottled young. Comparative analyses of these two young wines reveal that the values of all parameters decrease more significantly in the case of the white sample. In terms of organoleptic analysis, the cold treatment of young wines enhances the aroma expression, the flavor persistence and specific color for this type of wine. The conductivity values decrease in average with 18% and the total polyphenol index with 35%.

According to data presented in Table 1 the ionic strength (μ), the activity coefficients (γ_1, γ_2) for monovalent (K^+, HT^-) and bivalent ions (T^{2-}) were calculated. Bassed on these calculations were determined the parameters: the concentration product (PC), the thermodynamic product (PCT) and thermodynamic solubility product (PST) of KHT and its evolution – shown in Table 2.

The results included in Table 2 relieved the oversaturating stage in KHT of initial studied samples, values of PC for white wine $194.8 \cdot 10^{-6}$ mol^2/L^2 and $215.1 \cdot 10^{-6}$ mol^2/L^2 for red one, correspondingly. These values were 9 and 7 times higher than the PS at minus 4°C so the wine samples are in a risk area, it may be out of metastable equilibrium resulting the precipitation of KHT even at the temperature of 20°C (1.23 and 1.06 value of ratio PC/PS at 20°C). As a result of tartaric wine stabilization the ion bitartrate content in samples decreased in the range $2.7 \div 3.54 \cdot 10^{-3}$ mol/L and the concentration product diminished with 96.3 and $111.2 \cdot 10^{-6}$ mol^2/L^2. Theoretical saturation temperature of potassium bitartrate has decreased from 18 to 10°C in white sample and 21 to 13°C respectively for that red.

Table 1

Physico-chemical characteristics of the wine samples

№	Parameters	Wine sample					
		White wine			Red wine		
		Initially	Stabilized by chill-proofing	Stabilized by contact seeding	Initially	Stabilized by chill-proofing	Stabilized by contact seeding
1	Alcoholic degree, % v/v	12.62	12.48		10.25	10.18	
2	pH	3.13	3.08	3.06	3.30	3.20	3.22
3	Total acidity, g/L $C_4H_6O_6$	7.82	6.80	6.72	8.43	7.52	7.6
4	Volatile acidity, g/L CH_3COOH	0.42	0.48		0.52	0.54	
5	Content of tartaric acid, g/L	2.62	1.62	1.58	2.07	1.48	1.46
6	Content of potassium, mg/L	920	713	682	1070	894	821
7	Color intensity, $A_{420\ nm}$	0.092	0.048	0.042	1.483	1.345	1.121
8	Total polyphenol index, mg/L	148.76	86.31	82.54	1498.11	1076.47	1002.63
9	Conductivity at 20°C, μS/cm	1988	1670	1620	2066	1702	1684
10	Sensory analysis, points	7.7	7.8		7.9	8.0	8.0

During the cold stabilization has been not realized an excessive reduction of the analyzed parameters due to their buffer capacity as well as the PC is 3-4 times higher than PS at minus 4°C. This fact describes a correlation between PC and PS of samples, so the speed of formation and growth of KHT crystals are inhibited by the remaining colloidal compounds in wine system. So the analyzed samples are not prone to tartaric precipitation although PC is 3-4 times higher than PS.

The levels of the thermodynamic parameters reductions of wine samples have been expressed in % and are shown in Fig. 2. The comparative analysis of the two applied methods to ensure wine tartaric stability has revealed that the decrease of all parameters is more significant in the case of contact seeding procedure, in comparison with conventional cold stabilization.

This difference is ranging between 2.6 and 3.5% of wine samples, this permits to recommend the contact seeding procedure for the wine tartaric stabilization, in order to achieve young wines with pronounced organoleptic characteristics and stable thermodynamic parameters.

Table 2

Thermodynamic indices of tartaric crystallization in wine samples

№	Parameters	Wine sample					
		White wine			Red wine		
		Initially	Stabilized by chill-proofing	Stabilized by contact seeding	Initially	Stabilized by chill-proofing	Stabilized by contact seeding
1	Theoretical saturation temperature, ºC (± 0.19)	18.6	10.8	10.2	21.04	13.14	13.03
2	Content of ion bitartrate, 10^{-3} mol/L (± 1.72)	8.28	4.83	4.74	7.86	5.16	5.09
3	Concentration product (PC), 10^{-6} mol^2/L^2 (± 52.9)	194.8	88.6	83.6	215.1	118.8	116.4
4	Solubility product (PS) at minus 4°C, 10^{-6} mol^2/L^2 (±0.21)	21.27	21.01	21.48	29.03	28.48	28.60
5	Solubility product (PS) at 20°C, 10^{-6} mol^2/L^2 (± 1.3)	159.09	157.15	157.53	202.61	200.63	199.65
6	Ratio PC/PS at temperature minus 4°C	9.16	4.22	3.89	7.41	4.17	4.07
7	Ratio PC/PS at temperature 20°C	1.23	0.56	0.53	1.06	0.59	0.58

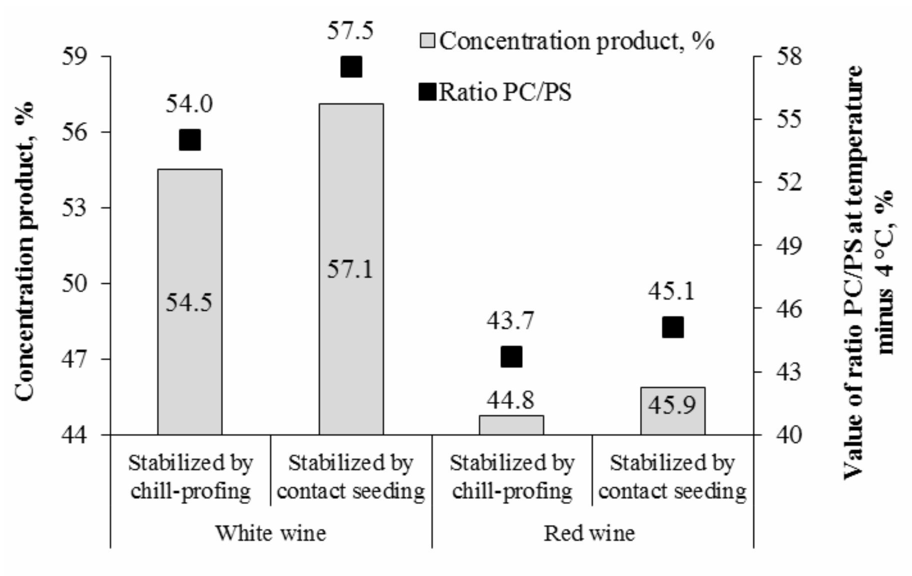


Fig. 2 – The decrease value of same thermodynamic parameters into wine samples, expressed in percentages and reported to the initial value.

Mathematical processing of the afore-presented results in Table 1 through an empirical model allowed establishing the influence of four determinant factors on theoretical saturation temperature. This dependence represents a polynomial equation (n = 2) of determined factors (X_1-X_4) in following form for white wine Chardonnay variety:

$$Y_{mod} = 42.07 - 50.567 \cdot X_1 + 0.3906 \cdot X_2 - 0.481 \cdot X_1 \cdot X_2 + 16.5685 \cdot X_1^2 - 0.00034 \cdot X_2^2 + 0.000418 \cdot X_1 \cdot X_2^2 + 0.1576 \cdot X_1^2 \cdot X_2 - 0.00014 \cdot X_1^2 \cdot X_2^2. \quad (1)$$

$$Y_{mod} = 2822.8 - 1797.6 \cdot X_3 + 10.58 \cdot X_4 - 6.74 \cdot X_3 \cdot X_4 + 287.2247 \cdot X_3^2 - 0.27854 \cdot X_4^2 + 1.077682 \cdot X_3^2 \cdot X_4 + 0.178 \cdot X_3 X_4^2 - 0.02833 \cdot X_3^2 \cdot X_4^2. \quad (2)$$

where: Y_{mod} – mathematical value of theoretical saturation temperature, ºC;
X_1 – content of tartaric acid, g/L;
X_2 – content of potassium, mg/L;
X_3 – value of pH, units;
X_4 – temperature of treatment, ºC;

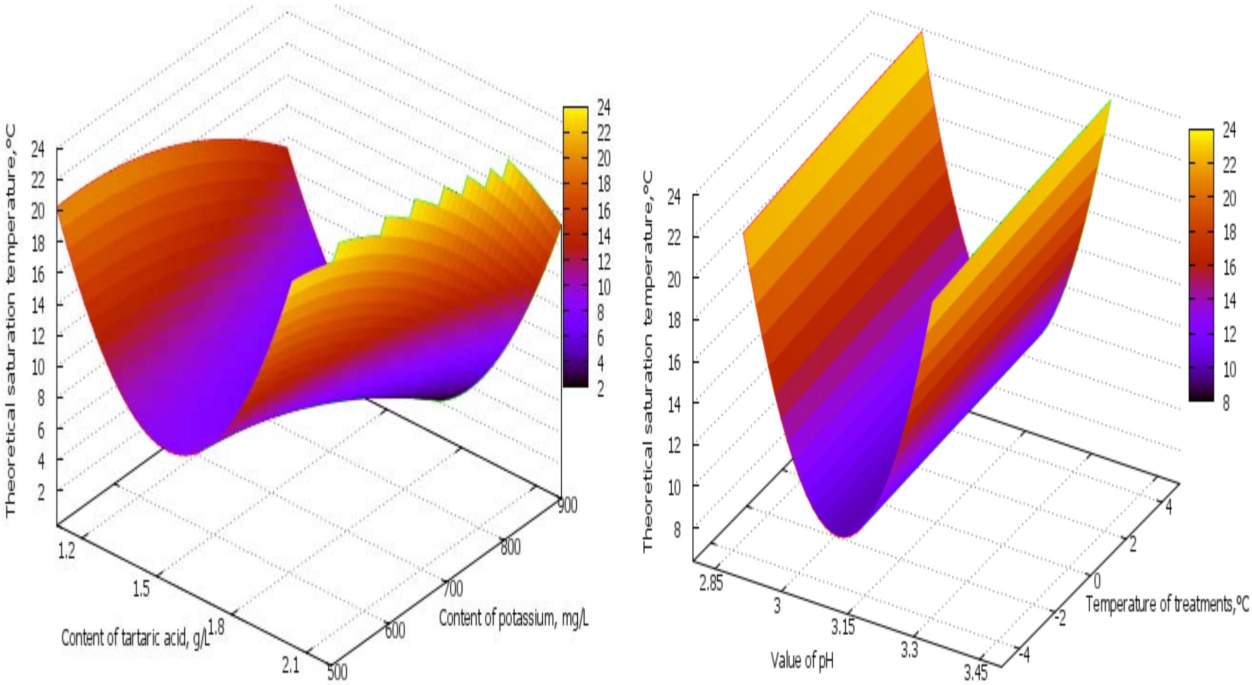


Fig. 3 – 3D interpretation of bifactorial dependence of theoretical saturation temperature into white wine Chardonnay variety.

In order to determine the optimal conditions for tartaric stabilization of wine samples in base of mathematical model (expressions 1 and 2) was represented its 3D interpretation using Gruplot 5.0 program selecting the variation range of each factor (Fig. 3).

The tartaric stability of wine is established then tartaric crystals are missing and a minimum of saturation temperature value. According to representation of Fig. 3, a minimum saturation temperature value is recorded at negative temperatures, with a content of tartaric acid within 1.4–1.6 g/L and the pH value between 3.08 and 3.15 units.

CONCLUSIONS

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 the perceived wine quality. During cold stabilization the total acidity value has increased in middle with 21%, the color intensity values were halved into the white sample and 25% for the red one. Also, the decrease of conductivity values at 20°C is range in limits of 318-382 μS/cm.

According to the achieved results, the cold stabilization reduces the values of concentration product of samples in the limits of 44.77÷57.1% of initial values. Also, the contact seeding is the most efficient procedure of wine tartaric stabilization, due to the present of KHT micro-crystals in the wine volume. As a result of applying this procedure young wines with pronounced organoleptic characteristics and stable thermodynamic parameters may be obtained.

The optimum conditions in tartaric stabilization of young whines include: the cold treatment at negative temperature, the content of tartaric acid within 1.4–1.6 g/L and the pH value between 3.08 to 3.15 units.

Generally, the cold treatment is, thus, adapted to each wine according to its specific instability, under conditions ensuring that there are no excessive alterations in its chemical composition. Further research is required to assess the effectiveness in different types of wine, especially tannic red wines and sweet ones which have particularly complex colloidal structures.

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