EFFECT OF DIFFERENT CHEMICAL ADDITIVES ON THE TARTARIC STABILIZATION OF YOUNG WINES

Sturza R.¹, *Covaci E.², Prida I.³

¹Technical University of Moldova, ²Institute of Chemistry, Academy of Sciences of Moldova, ³SRL Company "Oeno–Consulting", **Covaci E.: e-mail: covaci_ecaterina@yahoo.com**

Abstract: According to recent literature, the administration of additives that inhibit crystallization of tartar is highly recommended for application in winemaking. The present work was undertaken to verify the effect of chemical and natural additives on the potassium bitartrate stability and composition of 2 types of young wines. According to the data we found that the used additives inhibit potassium bitartrate crystallization at different doses between 10 and 60 g/hl. In conclusion, we recommend the use of chemical additives – carboxymethylcellulose (CMC), metatartaric acid (MetA) and mannoproteins (MP) in young wines to prevent possible tartaric precipitation. Recommended doses are: CMC at 2 g/hl, MP at 30–40 g/hl and MetA at 10 g/l.

Key words: young wines, bitartrate crystallization, chemical and natural additives

Introduction

Wine must not only be clear at the time of bottling but also preserve its clarity during aging and storage for an indefinite period, whatever the temperature conditions. Besides the microbial problems and tartrate precipitations described elsewhere, turbidity detrimental to clear wine (precipitation of coloring matter and metallic casse) involves colloidal phenomena. Traditionally, stable clarity was acquired during a long period of barrel aging. Transformations and precipitation took place spontaneously in the wine and any deposit was eliminated before bottling. Wine was usually bottled in the area where it was consumed. For a number of years now, thanks to progress in enology, winemakers have been able to assess the risk of turbidity and implement appropriate preventive measures before bottling. A distinction should be made in terms of cellar work between two separate issues. The aim, on the one hand, is to obtain total clarity by appropriate methods and, on the other hand, to achieve stability by means of efficient treatments [1].

The objective of stabilization is to ensure longterm clarity and prevent deposits, whatever the temperature, oxidation or lighting conditions where the wine is stored. The chemical and biological mechanisms likely to cause turbidity or deposits are now well known and may be predicted by laboratory tests.

In young wines potassium bitartrate (KHT) is always present in supersaturating concentration and crystallizes spontaneously. Refrigeration is widely used for stabilization to prevent tartrate precipitation in these wines. Physical treatments can be used prior to bottling of the wine to prevent crystallization of tartrate salts. Cold stabilization is not always totally effective and the following additional treatments may be used to ensure complete stability. The alternative to physical treatments of young wines is to use additives which prevent the nucleation and/or the growth of KHT–crystals. Carboxymethylcellulose (CMC), metatartaric acid (MetA) belongs to the group of

chemical additives and mannoproteins (MP) to natural additive which interfere with KHT crystallization [2] - [5].

The present study was conducted in order to study the influence of different chemical additives (carboxymethylcellulose, metatartaric acid and mannoproteins) on the evolution of tartrate stability indices of young white and red wines. All the positive results, combined with the fact that they are easy to use, relatively inexpensive, and do not require special investments, led to their practical study taking into account that they are authorized in winemaking by the International Code of Oenological Practice [6].

Materials and Methods

Investigations have been conducted on two white and red wines obtained from *Chardonnay* and *Pinot Noir* variety of 2013 vintage. Experiments were carried out during september–december 2013, at the Oenology Research Centre of Technical University of Moldova and at the Oeno–Consulting SRL Company, Chisinau, Moldova.

Physico-chemical analyses of the wines were carried out on the alcohol content, total acidity, pH and others, using the methods presented in national and international standards [7]or literature and are shown in Table 1.

Initially, the wine samples have been treated with bentonite finning in order to ensure the protein stability (filtration after the bentonite treatments), followed by dosing the additives in different dose levels: CMC the dose range from 2 to 10 g/hl; MetA the dose was 10 g/hl and for MP from 15 to 60 g/hl.

Stabilizing additives requires a prior preparation of concentrated solutions. For CMC was prepared a solution of 40 g/l in warm water (45°C) and dosed in wine samples with intense mixing. A concentrated solution, at 200 g/l of metatartaric acid was prepared in cold water at the time of use and dosed at a concentration of 10 g/hl in wine samples. For the PM wine samples were pre–filtered, administered the corresponding doses of additive and filtered through 0,7 μ m membrane.

The determination of the degree of tartaric instability (DTI) is carried out at temperatures above minus 5 $^{\circ}$ C and calculated by the following expression:

$$DTI = \frac{LF_{init} - LF_{fin}}{LF_{init}} *100 \%$$
⁽¹⁾

where: LF_{fin} – conductivity of the sample after administration 5 g of KHT and intensive homogenization during 15 minutes, mS/cm;

 LF_{init} – initial conductivity of the sample, mS/cm.

To create the wine lots with DIT ranging from 22,72 to 4,1% was administered the KHT crystals in samples followed by storage in a conditioned room at 10–12 °C. Periodically, the wine samples have been tested for tartaric stability by a conventional process consisting of cooling the wines at a temperature near the freezing point for 2 days with the administration of the oversaturated solution of KHT and an intensive homogenization to induce KHT precipitation. At the end of period, the samples were analyzed visual and concluded the presence or absence of tartaric crystals. The test results, therefore, indicated the final stability of wine and presented a risk of tartrate precipitation. The samples of wines are considered to be stable, if the tartaric crystals are missing, if not

the wines are unstable and can be retreated.

Results and Discussion

The data concerning the main wine composition characteristics are presented in Table 1. Initially, the results show that the samples of wines present tartrate instability at average level, having a theoretical saturation temperature ranging between 14,60 and 17,06 °C.

	Table 1. Frysico-chemical characterization of the wines.							
	Name of determined parameters	Values of parameters determined						
№ crt.		White wine Chardonnay		Red wine Pinot Noir				
		variety		variety				
		Sample 1	Sample 2	Sample 1	Sample 2			
1	Ethanol (% v/v)	12,60	12,22	10,25	10,04			
2	Total acidity, g/l C4H6O6	6,72	6,9	7,5	7,0			
3	Volatile acidity, g/l CH ₃ COOH	0,42	0,45	0,52	0,48			
4	pH	3,13	3,27	3,30	3,12			
5	Content of Iron, mg/L	0,53	0,18	1,12	0,16			
6	Content of sulfur dioxide (free/total), mg/L	20/90,8	6,5/107	18/150	13/98			
7	Content of potassium, g/l	0,682	0,718	0,821	0,682			
8	Content of tartaric acid, g/l	2,41	1,86	1,65	1,42			
9	Color intensity, A _{420 nm}	0,098	0,089	1,483	1,364			
10	Total polyphenol index (TPI) mg/l	148,78	132,49	1498,12	1292,67			
11	Antioxidant capacity, Trolox mg–ech/ml	0,016	0,014	0,340	0,282			
12	Conductivity at 20°C, µS/cm	1780	1698	1750	1820			
13	Theoretical saturation temperature, °C	14,60	14,91	16,04	17,06			
14	Type of instability manifested	Crystalline and protein instability						
15	Organoleptic analysis, points	7,8	7,9	7,8	7,8			

Table 1. Physico-chemical characterization of the wines.

The filtered wine samples were separated into different lots where various concentrations of additives were administered. The sample of wine stored at 10–12°C in conditioned room were tested for tartaric stability and the results of the study and the dose administered in each wine samples are summarized in Table 2.

MTFI-2014

N⁰ crt.	Type of wines	Dose of additive, g/hl	DTI, %	Visual observation of potassium crystallization after 6 days at – 5°C, day
1	White wine 1 added MP	0		1
		15	22,72	4
		25		4
		60		6
2	White wine 2 added MP	15	20,5	3
		60		8
3	White wine 1 added MP	0	14,25	9
		15		48
		30		64
		45		88
4	White wine 1 added MP	40	7,6	110
5	White wine 2 added CMC	10	19,25	32
6	White wine 2 added MetA	10	7,6	100
7	White wine 2 added CMC and	2 and	4,1	>100
	MetA	10		
8	Red wine 1 added MP	45	16,24	16
9	Red wine 1 added MetA	10	12,67	84
10	Red wine 1 added MetA and MP	10	11,43	160
		25		
11	Red wine 2 added CMC	2	12,6	50

Table 2. Tartrate stabilization of wine samples by addition of various additives.

The values obtained and presented in Table 2 indicate the effectiveness of protective colloids, even if they do not necessarily correspond to the instability temperatures. According to the data we found that the used additives inhibit potassium bitartrate crystallization at different doses between 2 and 60 g/hl. The effectiveness of chemical additives seems to vary according to the type of wine, but especially in relation to the presence of protective colloids and tartaric salts. However, in wines with high DTI a larger quantity of additives apparently increased the stabilizing effect.

The addition of metatartaric acid, however, reduced considerably the crystallization temperature but when the temperature is higher 20 °C the hydrolysis of metatartaric acid takes place in wine, and loses its effectiveness, while adding tartaric acid may even facilitate potassium bitartrate crystallization. The treatment is adapted to each wine according to its specific instability, under conditions ensuring that there are no excessive alterations in its chemical composition described in Table 1. The modifications in wine composition remain within an acceptable range and ensure stability. Under the same conditions, wines with CMC, MP and MetA are stable and have a durable protective effect on the tartrate crystallization.

In order to evaluate the stabilizing effect of additives of different doses it was studied the white wine with the following parameters: DTI - 7,6%, ethanol 12,6 % v/v and storage 90 days at 12–14 °C. Results of the test are shown in the following diagram displayed in Figure 1.

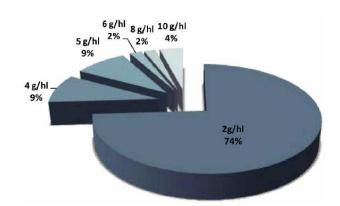


Fig. 1. Percentage of stabilized wine (without tartaric crystals) in dependence of the dose administrated CMC (visual observation of the white wine after 6 days at -5° C).

The effectiveness of CMC is due to its property of significantly reducing the growth rate of crystals, at the dose of 2 g/hl reduces crystal growth by a ratio of 74 % and at the dose 10 g/hl only 4 %. However, larger quantities of CMC in wines apparently reduced the stabilizing effect.

Generally, during stabilization with chemical additives have been observed the following consequences on the wine samples after the treatments:

- ➢ slight opalescence due to the high esterification number of metatartaric acid;
- reduction of the color intensity on average 9 % by the carboxymethylcellulose;
- ▶ increase of the color intensity of 4,4% compared to dose 2 g/hl for mannoproteins.

The effectiveness of MetA, CMC and MP is due to its property of significantly reducing the growth rate of crystals. All these positive results, combined with the fact that they are easy to use, relatively inexpensive, and do not require special investments, lead to their authorization for use in winemaking.

Conclusion

Tartrate solubility is reduced by the presence of ethanol, but precipitation is partially inhibited by colloidal substances that coat the crystal nuclei and prevent them from growing. For this reason, wines, particularly young wines, are likely to produce crystal deposits several months after fermentation.

In conclusion, we recommend the use of chemical additives – carboxymethylcellulose, metatartaric acid and mannoproteins in young wines to prevent possible tartaric precipitation during storage as long as they will not be cooled to a lower temperature than that of the treatment and the colloidal structure will not significantly change. Recommended doses are: CMC at 2 g/hl, MP at 30–40 g/hl and MetA at 10 g/l. Concerning metatartaric acid, it is therefore recommended to be added before the final clarification and to prepare the metatartaric acid solutions for treating wine just prior to use. Also, metatartaric acid is recommended to be used in wines with cold bottling, because the high–temperature bottling would reduce its effectiveness.

Further research is required to assess the effectiveness in different types of wine, especially tannic red wines, which have a particularly complex colloidal structure.

References

- Saint Pierre B., Batlle J-L., Escudier J-L. et Moutounet M. L'instabilité tartrique des vins; problématique, évaluation, méthodes et techniques de stabilisation. In "OEnologie fondements scientifique et technologiques". C. Flanzy, Ed. Lavoisier Tech et Doc Paris, **1998**, 921–935.
- [2] Ribereau–Gayon P., Yves Glories, Maujean A. And Dubourdieu D. Handbook of enology. The chemistry of wine. Stabilization and treatments. Vol 2, Ed. John Wilei&Sons, England, 2006, 369–386.
- [3] Moutounet M., Bouissou D. et Escudier J.L. *Effet de traitement de stabilisation tartrique de vins rouges par une gomme de cellulose* (Carboxymethylcellulose). www. infowine.com N.6/2, **2010**.
- [4] Marchal R., Laigre M., Jeandet P., Robillard B. et Legras V. *Utilisation de CMC pour la stabilisation tartrique des vins blancs*. **2009**, Nr130, 18–19 et nr.133, 38–41.
- [5] Blateyron L. Evolution de l'effet de l'adjonction de mannoprotéines sur la stabilité tartrique des vins et la validité du test de stabilité tartrique. Rapport d'experimentation CPE/RLR, **2006**, 1–8.
- [6] Organisation international de la vigne et du vin, **2012**. *Code International des pratiques Œnologiques*. Edition, 298.
- [7] Office International de la Vigne et du Vin, **2005**. *Recueil des méthodes internationales d'analyse des vins et de moûts*. Édition Officielle, juin, Paris.