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Characterization, control and improvement of the cold treatment of Sherry wines

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Abstract

Cold treatment has been characterized on Sherry wines to adapt it to each type of wine and to improve its results. Rapid response conductivity measurements were used to control the process. Cold treatment leads to more rapid tartrate stability than usually used, and Fino, Manzanilla and Oloroso wines are stabilized in only one day. Medium and Cream wines need at least three days, but some of these wines are hardly affected by the treatment, as a result of their complex nature. Cold treatment can be carried out simultaneously with the fining process in Fino and Manzanilla wines, attaining the tartrate stability in five days.

Keywords: Tartrate stabilization; Cold treatment; Sherry wines; Saturation temperature; Minicontact test

1. Introduction

The tartrate stabilization process for wines has become widespread in the last 50 years and today it is applied to almost all wines before bottling (Ribereau-Gayon, Peynaud, Ribereau-Gayon, & Sudraud, 1977). Among the techniques used in this area, cold treatment is without doubt the most widely applied (Celotti, Bornia, & Zoccolan, 1999; Goertges & Stock, 2000; Gómez Benítez, Szekely Gorostiaga, Veas López, Palacios Macías, & Pérez Rodríguez, 2002; Guerif, 1993; Mourgues, 1993; Moutounet, Saint-Pierre, Batlle, & Escudier, 1997; Ribereau-Gayon, Glories, Maujean, & Dubordieu, 1998). Several modes of operation can be found for this technique but the method designated 'traditional cold treatment' is the most commonly used (Blouin, 1982) (henceforth this method is referred to as cold treatment). This technique involves cooling the wine down to a temperature close to its freezing point and storing it in isothermal tanks during a period of approximately one week (Ribereau-Gayon et al., 1977). This treatment is usually carried out after fining and filtration of the wine in order to facilitate the crystallization of potassium bitartrate (KHT).

There is a wide range of Sherry wines and these differ according to the ageing process used (biological or oxidative) and the composition of the blending (dry or sweet wines) (C.E., 1988; C.E., 1999; González Gordon, 1972; Jerez-Xérèz-Sherry, 1977; Martínez, Pérez, & Benítez, 1997; Pérez Rodríguez, 1991). These differences induce different behaviours during the tartrate stabilization treatments. The biological ageing of Fino and Manzanilla wines produces a decrease of the dry extract, a modification that facilitates the precipitation of KHT (Martínez de la Ossa, Caro, Bonat, Pérez, & Domecq, 1987). In contrast, the use of natural sweet wines and "colour wines" (obtained by flame-heating wines directly) as components of the blends for Medium and Cream wines (González Gordon, 1972) introduces a large quantity of colloids (Usseglio-Tomasset, Bossia, Delfini, & Ciolfi, 1980) which inhibit the precipitation of KHT (Gómez Benítez, Palacios Macías, Sánchez Pazo, & Pérez Rodríguez, 2002). Consequently, in these types of wine frequent troubles with stabilization arise which have not been definitively resolved.

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In Sherry wines it is especially important to have a reliable and rapid system to determine tartrate stability. The traditional method is to observe the formation of crystalline sediment in a sample stored at low temperature (Berta, 1993; Brugirard & Rochard, 1992; Colagrande, 1984). However, this method suffers from low reproducibility and is time consuming. Therefore, systems used today are based on rapid response conductivity measurements and these methods include the saturation temperature of the wine in potassium bitartrate (T_s) and the minicontact test (M_c) (Gómez, Palacios, Caro, & Pérez, 1999).

The time periods involved in the traditional treatments and control by the traditional systems are not well-suited to the current logistical needs, which demand minimum response times. Furthermore, the cold treatment process has high operational costs in terms of labour and energy, and these costs can rise to 0.76 euros/hl (Gómez Benítez et al., 2002).

The work described here was undertaken to characterize and improve the cold treatment of Sherry wines. The objective of the study was to gain an understanding of the effects of the treatment process for the different types of wine and to tailor the process for each specific type. The improvements were aimed at reducing the treatment duration and to simplify the operations involved.

2. Materials and methods

2.1. Methodology

A sampling was carried out in a commercial cellar during two years in order to determine the effect of the cold treatment on the composition and stability of the wine. Samples of different blends of wine were taken both before and after cold treatment and at least 24 samples of each type were obtained.

Another sampling was carried out in order to study the effect of a reduction in the length of the treatment. Six experiments were performed on each type of wine and samples were taken before treatment, after having passed through the refrigeration equipment, on a daily basis until the seventh day and, finally, after filtration.

Six treatments of Fino and Manzanilla wines were sampled in order to study the effect of cold treatment with simultaneous fining. The finings were performed with 10 g/hl of gelatine and 50 g/hl of bentonite.

These samplings were carried out in commercial cellars in the Sherry area (Denomination of Origin Sherry-Xérèz-Sherry and Manzanilla de Sanlucar de Barrameda).

2.2. Cold treatment

A standard cold treatment process was used by means of the refrigeration of the wine at a temperature close to its freezing point (between −6 and −8 °C) and storing it at this temperature during one week; the maximum increase in the wine temperature during the treatment is 2.0 °C/week.

An installation with a refrigeration capacity of 98 kW and a maximum flow of 7500 l/h was used. The storage tanks had a capacity of 23,000 l and were constructed from AISI 304 stainless steel. These tanks were covered with an insulating layer of 30 cm thickness and the maximum temperature increase in the wine during the treatment was 1.7 °C/week.

2.3. Determination of saturation temperature (T_s) and Minicontact test (M_c)

An automatic system was used to determine T_s and M_c values (Angele, 1992; Gaillard, Ratsimba, & Favarel, 1987) This system, which is based on the polythermal method, measures wine conductivity in two samples, a control and another sample with added KHT (4 g/l) (García Ruiz, Alcántara, & Martín, 1991). The first run is carried out at a heating rate of 2.7 °C/min and the second at 1.7 °C/min. The saturation temperature is the point at which the conductivities of the two samples are equal. The error in the T_s measurement, within the range of alcohol strengths of Sherry wines, is +0.30 °C (Gómez et al., 1999). This accuracy is suitable to control the process. In the minicontact test the wine, with 4 g/l of KHT added, is kept at a temperature of 0 ± 0.1 °C during a maximum time of 18 min. The result of the test is the decrease in the conductivity and this value is named M_c (Gómez et al., 1999).

2.4. Analytical determinations

European official methods of analysis were used to determine the pH and total acidity (C.E.E., 1990). The determination of potassium was carried out by flame emission photometry. The tartaric acid content was determined by HPLC, with UV detection at 214 nm (Frayne, 1986). Tartrate stability was measured by observing the formation of crystalline sediment in a sample stored at low temperature (−6 °C) during one week (Brugirard & Rochard, 1992).

All the determinations were carried out in duplicate, with the arithmetic means of the results presented.

2.5. Statistical analysis

A significance level of 95% was used to determine the confidence interval. The determination of the t Student factor was carried out in coupled samples with two-tailed distribution.

Table 1
Values of different parameters in traditional cold treatments of Sherry wines

Wine		pH		Titratable ac. (g/l tartaric acid)		Potassium (mg/l)		H_2T[a] (g/l)		T_s[b] (°C)		M_c[c] (μS/cm)	
		AM[d]	t[e]	AM[d]	t[e]	AM[d]	t[e]	AM[d]	t[e]	AM[d]	t[e]	AM[d]	t[e]
(a) Fino and Manzanilla													
C[f]		3.09 ± 0.02	1×10^{-21}	4.32 ± 0.09	5×10^{-11}	791 ± 31	1×10^{-13}	2.43 ± 0.07	4×10^{-20}	22.8 ± 0.6	1×10^{-25}	106 ± 26	1×10^{-7}
CT[g]		2.91 ± 0.01		3.82 ± 0.04		575 ± 11		1.66 ± 0.03		12.6 ± 0.3		2 ± 0.4	
(b) Oloroso													
C		3.17 ± 0.16	0.03	5.43 ± 0.12	0.11	600 ± 24	0.03	2.13 ± 0.10	1×10^{-3}	22.2 ± 0.31	3×10^{-4}	40 ± 2	3×10^{-5}
CT		3.07 ± 0.10		5.02 ± 0.16		443 ± 36		1.70 ± 0.08		15.7 ± 1.1		1 ± 0.5	
(c) Mediums A and B													
A	C	3.25 ± 0.05	0.11	4.76 ± 0.11	0.06	820 ± 35	2×10^{-3}	2.15 ± 0.18	3×10^{-4}	25.7 ± 0.9	7×10^{-6}	31 ± 4.5	5×10^{-5}
	CT	3.18 ± 0.03		4.46 ± 0.06		690 ± 22		1.49 ± 0.09		20.3 ± 0.6		4 ± 0.8	
B	C	3.11 ± 0.04	0.28	4.33 ± 0.09	0.06	715 ± 26	0.21	2.02 ± 0.15	0.21	20.3 ± 0.7	2×10^{-3}	9 ± 1.5	0.02
	CT	3.09 ± 0.02		4.23 ± 0.04		685 ± 17		1.91 ± 0.06		18.8 ± 0.4		3 ± 0.7	
(d) Creams A and B													
A	C	3.47 ± 0.05	0.23	4.00 ± 0.07	7×10^{-3}	900 ± 55	0.01	1.89 ± 0.21	0.04	26.3 ± 2.9	0.05	22 ± 11.3	0.27
	CT	3.43 ± 0.02		3.74 ± 0.13		777 ± 30		1.44 ± 0.07		21.4 ± 0.4		1 ± 0.4	
B	C	3.11 ± 0.10	0.69	4.00 ± 0.12	0.49	629 ± 48	0.71	1.75 ± 0.17	0.82	17.9 ± 0.9	0.28	1 ± 0.5	0.30
	CT	3.08 ± 0.09		4.00 ± 0.09		603 ± 25		1.66 ± 0.14		17.2 ± 0.8		1 ± 0.4	

[a] Tartaric acid.
[b] Saturation temperature.
[c] Minicontact test.
[d] Arithmetic mean and confidence interval.
[e] *t* Student factor.
[f] Control.
[g] Cold treatment.

3. Results and discussion

Cold treatment led to decreases in the pH, total acidity, potassium, tartaric acid, T_s and M_c, and these values changed in different ways depending on the type of wine (Tables 1 and 2). In all cases there was good correlation between the values of T_s (°C) and potassium (mg/l) (correlation coefficient: 0.992); therefore, this magnitude could be used as a control method for the treatment process. Likewise, a good correlation between the variation in T_s and the initial M_c value (μS/cm) (correlation coefficient: 0.96) is observed; consequently, M_c could be used as an indicator of the stabilization potential of the wine.

The largest decreases were observed in Fino wines (Table 1(a)) and, to a lesser extent, in Oloroso wines (Table 1(b)).

Medium and Cream wines have been separated into two groups (A and B) according to their composition. Wines of type B had a greater colloidal matter content than those of type A. This colloidal matter originated from sweet wines and colour wines when used in larger proportions during blending (Usseglio-Tomasset et al., 1980). Medium and Cream A-type wines (Table 1(c) and (d)) had a similar behaviour to Oloroso wines but, in contrast, the composition of Medium and Cream B-type wines changed only slightly during the treatment (Table 2). In both groups the decreases in the parameters under investigation were larger in Medium wines than in Cream wines.

This behaviour was confirmed by the t Student factor, which showed very small values in the Fino and Manzanilla wines and larger values in the other types of wine.

Plots of the T_s values versus time during the process were inherently different for the different types of wine (Fig. 1). The curves showed very pronounced initial decreases and subsequent stabilizations in Fino, Manzanilla and Oloroso wines. This situation was particularly remarkable in Fino and Manzanilla wines, because T_s decreases by 7.5 °C upon passing the wine through the refrigeration equipment. In Medium and Cream A wines, the graphs showed smaller initial decreases but the trend is maintained over longer periods. In Medium and Cream B wines the variations in the T_s values were very small.

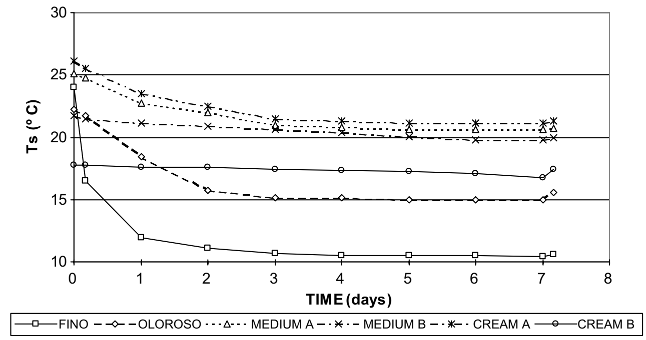

Fig. 1. Evolution of saturation temperature values during traditional cold treatment.

The behaviour patterns observed in terms of T_s were in direct relationship with the intensity of the inhibition phenomena of KHT crystallization caused by the components of the different wines, particularly the colloidal matter. In all the wines a slight increase of T_s was observed at the end of the treatment and this was due to some KHT redissolving during the earth filtration.

The parameter M_c showed a similar evolution behaviour as T_s, although the most pronounced variations were seen in the first few days (Fig. 2). Fino, Manzanilla and Oloroso wines were stabilized from the first day and Medium and Cream A wines from the third day (Table 3). Medium and Cream B wines were stable before treatment.

A relationship between wine stability and M_c value was observed in all of the wines studied here (Table 3, Fig. 2); when the M_c value was equal to or lower than 10 μS/cm the wine was stable for at least one week at 4 °C (Gómez et al., 1999).

Therefore, the length of the cold treatment process could be reduced to one day for Fino, Manzanilla and Oloroso wines, or three days for Medium and Cream A wines. On the other hand, the intensity of the treatment (in terms of time and/or temperature) of some of the Medium and Cream B wines could be reduced and others in this group could be not treated at all. This

Table 2
Variations in the concentrations of potassium, tartaric acid, and saturation temperature during traditional cold treatment

Wine		Potassium (meq/l)	Tartaric acid (meq/l)	T_s[a] (°C)
Fino and Manzanilla		5.52	5.1	10.2
Oloroso		4.01	3.89	6.5
Medium	A	3.32	3.20	5.4
	B	0.77	0.73	1.5
Cream	A	3.14	3.01	4.9
	B	0.66	0.60	0.7

[a] Saturation temperature.

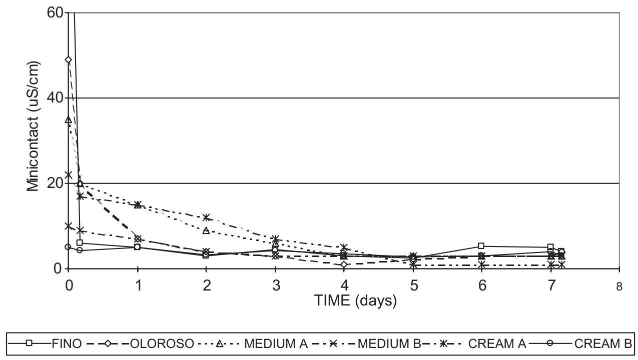

Fig. 2. Evolution of M_c values during traditional cold treatment.

should be confirmed in each case by determining the M_c value.

The fining process, when performed simultaneously with cold treatment, produced an additional inhibition to that caused by the components of the wine itself. Therefore, it was only feasible to apply the fining process to Fino and Manzanilla types, which represent 40% of Sherry production. Under these conditions the decreases in the T_s and M_c values were less marked than the corresponding values in the absence of the fining agent (Fig. 3(a) and (b)). Nevertheless, at the end of the treatment there were no appreciable differences between them, and the tartrate stability was achieved on the fifth day of the treatment process (Table 4).

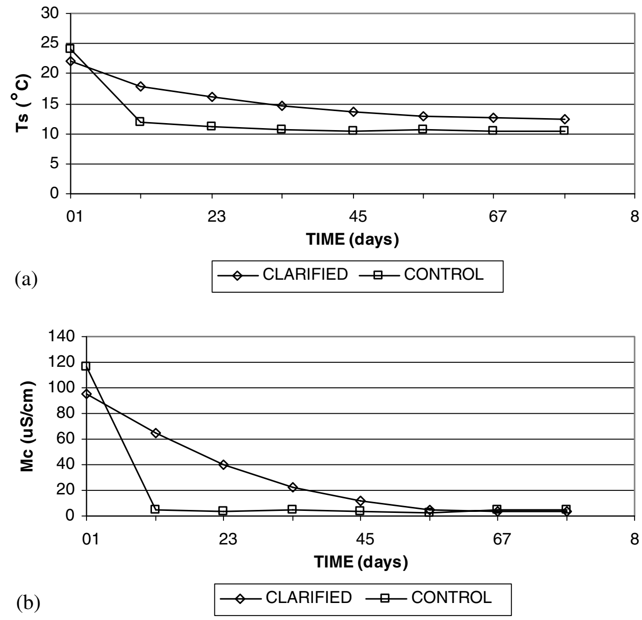

Fig. 3. Evolution during traditional cold treatment with simultaneous fining in Fino and Manzanilla wines. (a) Saturation temperature, (b) minicontact test.

Table 3
Tartrate stability test during the traditional cold treatment

Wine	Treatment duration (days)									
	0	RE[a]	1	2	3	4	5	6	7	F[b]
Fino and Manzanilla	1	>7	>7	>7	>7	>7	>7	>7	>7	>7
Oloroso	3	6	>7	>7	>7	>7	>7	>7	>7	>7
Medium A	4	5	7	7	>7	>7	>7	>7	>7	>7
Medium B	7	>7	>7	>7	>7	>7	>7	>7	>7	>7
Cream A	5	5	6	7	>7	>7	>7	>7	>7	>7
Cream B	>7	>7	>7	>7	>7	>7	>7	>7	>7	>7

Values in days without sediment.
[a] After refrigerator equipment.
[b] After filtration.

Table 4
Evolution during the cold treatment with simultaneous fining in Fino and Manzanilla wines

	Treatment duration (days)							
	0	1	2	3	4	5	6	7
pH	3.21	3.15	3.13	3.12	3.11	3.10	3.10	3.10
Titratable ac. (g/l)	4.77	4.49	4.36	4.3	4.27	4.25	4.24	4.24
Potassium (mg/l)	747	657	620	589	565	553	545	538
Tartaric acid (g/l)	2.65	2.30	2.11	2.00	1.93	1.90	1.89	1.88
T_s (°C)[a]	22.1	17.9	16.2	14.7	13.6	13.0	12.6	12.3
M_c (μS/cm)[b]	95	65	40	22	12	5	4	3
Stability test (days)	1	2	3	5	6	>7	>7	>7

[a] Saturation temperature.
[b] Minicontact test.

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References

Angele, L. (1992). Stabisat: Contrôle de la stabilité tartrique et gestion de la production. *Revue des Oenologues, 65*, 43–47.

Berta, P. (1993). Measurement of tartrate stability in wine. *Vignevini, 11*, 21–46.

Blouin, J. (1982). Les techniques de stabilisation tartrique des vins par le froid. *Connaissance Vigne Vin, 16*(1), 63–77.

Brugirard, A., & Rochard, J. (1992). Prévention des précipitations tartriques. In *Aspects pratiques des traitements thermiques des vins* (pp. 74–105). Chaintré, France: Bourgogne-publications.

C.E. (1988). Reglamento 4252/88 de 21 de diciembre de 1988 relativo a la elaboración y a la comercialización de los vinos de licor producidos en la Comunidad. *D.O.C.E.* L 373, pp. 59–65.

C.E. (1999). Reglamento 1493/1999 del Consejo de 17 de Mayo de 1999 por el que se establece la organización común del mercado vitivinícola. *D.O.C.E.* L 179, pp. 1–84.

C.E.E. (1990). Reglamento 2676/90 por el que se determinan los métodos comunitarios aplicables al sector del vino. *D.O.C.E.* L 272, pp. 1–192.

Celotti, E., Bornia, L., & Zoccolan, E. (1999). Evaluation of the electrical properties of some products used in the tartaric stabilization of wines. *American Journal of Enology and Viticulture, 50*, 343–350.

Colagrande, O. (1984). L'impiego del freddo per la stabilizzazione dei vini nei confronti del bitartrato de potassio. In Chiarotti (Ed.), *Proceedings of the Symposium Vino, bevanda e alimento*, Pinerolo, Italy (pp. 183–192).

Frayne, R. F. (1986). Direct analyis of major organic components in grape must and wine using high performance liquid chromatography. *American Journal of Enology and Viticulture, 37*(4), 281.

Gaillard, M., Ratsimba, B., & Favarel, J. L. (1987). Procédé et installation pour déterminer la température de saturation d'un sael naturel dans le vin. *Demande de brevet d'invention.*, no. publication 2611910, no. enregisrement 87 027381987.

García Ruiz, J. M., Alcántara, R., & Martín, J. (1991). Evaluation of wine stability to potassium hydrogen tartrate precipitation. *American Journal of Enology and Viticulture, 42*, 336–340.

Goertges, S., & Stock, R. (2000). Crystals in wine. Crystal stabilization and stability control. *Deutsche-weinmagazin, 2*, 24–28.

Gómez, J., Palacios, V. M., Caro, I., & Pérez, L. (1999). Puesta a punto de un método de predicción rápida de la estabilidad tartárica en vinos de Jerez. In *Proceedings of 5th Congreso Nacional de Enólogos*. Mérida, Spain (pp. 135–140).

Gómez Benítez, J., Szekely Gorostiaga, P., Veas López, R., Palacios Macías, V. M., & Pérez Rodríguez, L. (2002). *Tecnología del vino, 6*, 45–49.

Gómez Benítez, J., Palacios Macías, V. M., Sánchez Pazo, J. A., & Pérez Rodríguez, L. (2002). *European Food Research and Technology, 214*(5), 418–422.

González Gordon, M. (1972). *Sherry. The noble wine*. London: Wine & Spirit Publications.

Guerif, G. (1993). L'électrodialyse appliquée à la stabilisation tartrique des vins. *Revue des Oenologues., 69S*, 39–42.

Jerez-Xérèz-Sherry (1977). Orden por la que se reglamentan las denominaciones de origen Jerez-Xérèz-Sherry y Manzanilla de Sanlucar de Barrameda y su consejo regulador. *B.O.E.* p. 113.

Martínez, P., Pérez, L., & Benítez, T. (1997). Velum formation by flor yeast isolated from Sherry Wine. *American Journal of Enology and Viticulture, 48*, 55–61.

Martínez de la Ossa, E., Caro, I., Bonat, M., Pérez, L., & Domecq, B. (1987). Dry extract in sherry and its evolution in the aging proces. *American Journal of Enology and Viticulture, 38*(4), 321–325.

Mourgues, J. (1993). Utilisitation des résines échangeuses d'ions. *Revue des Oenologues, 69S*, 51–54.

Moutounet, M., Saint-Pierre, B., Batlle, J. L., & Escudier, J. L. (1997). Le stabilisateur tartrique: principe et description du procédé. *Revue Française d'Oenologie, 162*, 15–17.

Pérez Rodríguez, L. (1991). La crianza del vino de Jerez. *Vitivinicultura, 9*, 19–22.

Ribereau-Gayon, J., Peynaud, E., Ribereau-Gayon, P., & Sudraud, P. (1977). In Dunod (Ed.), *Sciences et techniques du vin. T4. Clarification et stabilisation. Matériel et installations*, Paris (pp. 255–264).

Ribereau-Gayon, P., Glories, Y., Maujean, A., & Dubordieu, D. (1998). In Dunod (Ed.), *Traité d'oenologie. T2. Chimie du vin. Stabilisation et traitments*, Paris, France.

Usseglio-Tomasset, L., Bossia, P. D., Delfini, C., & Ciolfi, G. (1980). I vini Recioto e Amarone della Valpolicela. *Vini d'Italia, 125*, 85–97.