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ORIGINAL PAPER

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Industrial development of proton exchange for tartrate stabilization of sherry wines

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Abstract Proton exchange and cold treatment were applied for tartrate stabilization of three types of sherry wines (fino, medium and cream) to determine their effectiveness and compare their results. Firstly, proton exchange was studied on a laboratory scale, to elucidate its effects on the nature of the wine and to choose how to act in industrial experiments. It has been proven that the treatment efficacy depends only on the initial cation load of the wine and that it also produces a considerable decrease in wine oxidizability, which can be up to 1/3 of the original. In proton exchange trials on an industrial scale no noticeable differences were observed with those on a laboratory scale, verifying that to obtain an appropriate tartrate stability it is necessary to mix a proportion of 15% of treated wine for fino sherry, and 10% in the cases of medium and cream sherries. No important differences in the effects of the two techniques on the pH or sensorial characteristics of the wine have been observed. Likewise, it has been shown that cold treatment has a larger effect on the colour intensity of the wine than proton exchange, and that it presents a reduced effectiveness in cream sherries.

Keywords Tartrate stabilization · Proton exchange · Sherry wines · Cold treatment

Introduction

In the Sherry area the most widespread system for tartrate stabilization is discontinuous cold treatment without seeding [1], although it is sometimes used with seeding [2], and by continuous treatment [3]. Cold treatment produces a remarkable stabilizing effect in white wines, but it presents some difficulties in wines with complex colloidal compositions, as in some red and naturally sweet wines [4, 5]. Furthermore, cold treatment has high costs and is time consuming. Other methods for tartaric stabilization also used are the addition of metartaric acid [6, 7, 8] and electrodialysis [9, 10, 11]. Ion exchange, with cation resins in proton form placed in a column, is also used for tartrate stabilization of wines [12, 13, 14]. During the treatment, the wine cations are substituted by the protons fixed in the resin. The volume of eluted wine depends fundamentally on the cation load of the wine, and is independent of its physico-chemical conditions [15]. By continuing the treatment, cations previously retained in the resin are eluted according to a growing order of affinity which is determined by their activity coefficients [16]. As the effect of proton exchange treatment on concentrations of cations participating in the equilibria of tartrate stability is very large, exchanged wine is usually mixed in a certain proportion with untreated wine to obtain stable wine. In experiments on stabilization of white, rosé and red table wines, good results have been obtained with mixtures of treated wine between 10% and 20%, whereby a maximum decrease of pH of 0.2 units has been observed [14, 17]. Proton exchange has also been used for acidification of musts [18].

Wine treatment by proton exchange has been accepted by the Office International de la Vigne et du Vin [19], and authorized by the EU for the production of rectified concentrated musts [20, 21].

Sherry wines are liqueur wines produced in the south of Spain [20, 22], whose production has been widely described in the literature [23, 24, 25], with a wide range of wine types differing in their natures and residual sugars

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content [26]. Concerning their tartrate stability, one of their main particularities is the use of natural sweet wines, because their high colloids content inhibits potassium hydrogen tartrate (KHT) crystallization during the later tartrate stabilization.

The objective of this work was to study the application of the proton exchange technique to tartrate stabilization of sherry wines and to compare its results with those of the cold treatment, verifying their effectiveness for different types of wine.

Materials and methods

Description of proton exchange and cold treatment plants. In all the instances of proton exchange a strong acid cationic resin was used. It consisted of a matrix of polystyrene reticulate with divinylbenzene (8%), with sulphonic functional groups. In laboratory experiments, a glass column of 500 ml was used with a resin bed of 200 ml. In the industrial experiments a column made of stainless steel AISI 316-L, with a content of 1 m^3 of resin and accessories, valves and flowmeters for its appropriate control was used [18]. For the cold treatments, a standard system was used, where the wine is refrigerated to a temperature close to its freezing point and kept at this temperature for 1 week. The installation had a refrigeration capacity of 85,000 frigories and the insulated storage tanks a volume of 23,000 l.

Operation conditions and experiments. Proton exchange treatment was tested for fino (dry), medium (40 g/l of residual sugars) and cream (100 g/l of residual sugars) types of sherry wines. In the laboratory experiments, wine was eluted until the effluent pH equalled the feeding pH, carrying out a sampling each 2.5 resin volumes while the pH was constant, and each 0.5 resin volumes when the pH began to vary. In the experiments on an industrial scale the treatment was finished when the effluent pH began to increase; this way a maximum treatment effectiveness was obtained, a sampling being carried out each 1.7 resin volumes during the whole treatment. The flow used in all the experiments was 10 l/h /l resin and the resin regeneration was made with 4 l of 5% H_2SO_4/l of resin.

Cold treatment was applied to the same wines; this allowed comparison of the results of the two techniques. The industrial experiments were performed in a commercial cellar of the sherry area (Denomination of Origin Jerez-Xérèz-Sherry y Manzanilla de Sanlucar de Barrameda).

Analytical determinations. For the determination of pH and total acidity, the European Official Methods of Analysis were used [27]. The determination of Na and K was carried out by flame emission photometry, and that of Ca, Mg and Fe by atomic absorption spectrophotometry, using the Pye Unicam model SP9. The electrical conductivity was measured with a Crison GLP 32 conductimeter with temperature compensation. Tartaric acid was determined according to the Rebelein method [28], using a Shimadzu MPS 2000 spectrophotometer. As a measurement of the total content of phenolic compounds, the absorbance at 280 nm (dilution 1/10) was determined, and as a measurement of wine colour intensity, the absorbance at 420 nm was used. To measure tartrate stability, the sediment formation in a sample stored at –6 °C for 1 week was observed [29]. To determine the oxidative stability, the absorbance increase at 420 and 470 nm of a wine sample saturated with air, closed tightly and heated at 45 °C for 10 days was measured [30]. All the determinations were carried out twice, and the arithmetic means of the results are presented.

Sensorial analysis. Sensorial analysis was carried out by a team of five expert tasters from the cellar where the experiments were carried out. The tasting was carried out blind, according to the bilateral coupled technique [31], and the attributes of the wine corresponding to the senses sight, smell and taste were valued, each one being scored from a minimum of 0 to a maximum of 5 points. Furthermore, a global preference valuation of each type of wine was carried out.

Results and discussion

Proton exchange experiments on a laboratory scale

Effects on the ionic composition of the wine. To study the effect of the proton exchange on the ionic composition of the wine, pH, electrical conductivity and concentrations of the cations K^+, Na^+, Ca^{2+}, Mg^{2+} and $Fe^{+2/+3}$ in the eluted wine for the three types of wine under consideration were determined. The results for the fino wine are presented in Fig. 1, and are similar to those for the medium and cream wines. As a general rule, two phases can be observed; during the first one (load phase), the concentrations of cations considered and the effluent pH decreased from the beginning of the treatment, reaching low values (pH<2 and cations concentrations of a few milligrams per litre), and remained constant during this phase. The electrical conductivity suffered an important initial increase because of released protons, and after a reduction due to the passage of the elution front, it stabilized during the rest of the phase.

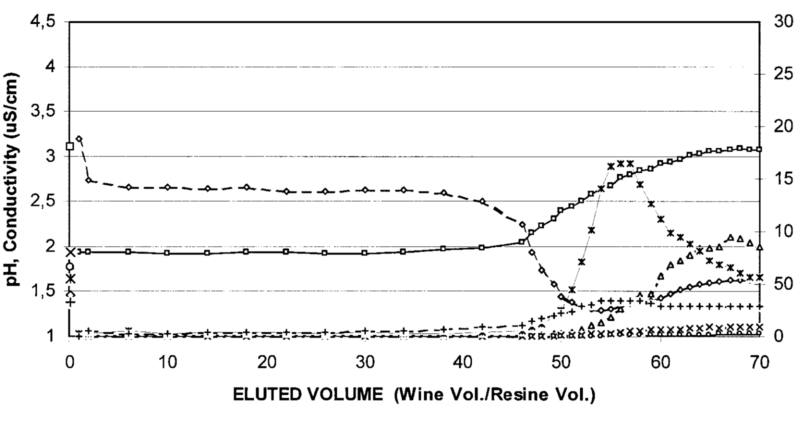

Fig. 1 Variations in pH, conductivity and cations concentrations in the wine effluent of the proton exchange column (laboratory scale). Values corresponding to the feeding wine are represented at eluted volume 0, being constant during the whole experiment

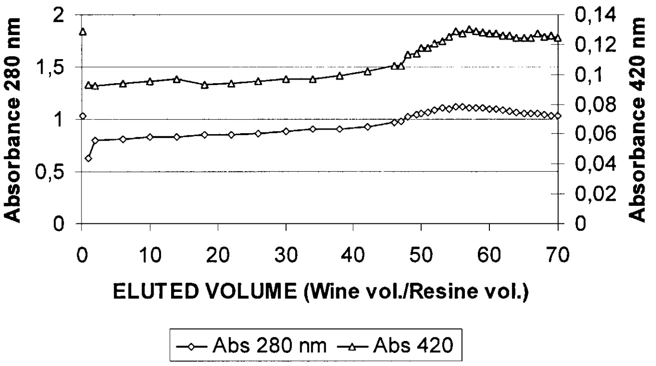

Fig. 2 Variations of the absorbances at 280 nm and 420 nm in the effluent of the proton exchange column (laboratory scale).Values corresponding to the feeding wine are represented at eluted volume 0, being constant during the whole experiment

Table 1 Duration of the load phases of proton exchange treatment of different types of sherry wines. *vol* Volume

	Fino	Medium	Cream
Cycle (eluted vol./resin vol.)	40	30	30
Cations sum (meq/l)	28.5	34.0	35.9

Following this, the pH of the eluted wine increased until it reached the feeding pH, and the fixed cations were eluted (discharge phase). Their order of elution ($H^+ < Na^+ \approx Fe^{+2/+3} < K^+ < Mg^{+2} < Ca^{+2}$) in general agrees with their activity coefficients. In this phase, the electrical conductivity showed a reduction, coinciding with the increase in the pH, and a later increase due to the cations' elution. In the final stage of the cycle, the active functions of the resin would be mostly fixed with the ions Ca^{+2} and Mg^{+2}, and the column would already be inactive for tartrate stabilization. This evolution is similar to that presented in [13]. The described phenomena were similar in the different types of wine tested, and were not influenced by the nature of the wine. Differences in the duration of load phases were observed and they are inversely related to the sum of equivalents of the involved cations (Table 1).

Effects on the phenolic content and the wine colour. An initial decrease in the absorbances at 280 nm and 420 nm was observed, followed by a slow increase during the load phase and a quicker increase during the discharge phase, until similar values to the feeding wine were reached (Fig. 2). That is because the resin exercises a certain absorbent action on the wine's phenolic compounds [16].

Table 3 Tartaric stability tests of mixtures in different proportions of treated and untreated wine by proton exchange. Values are the number of days for the sediment to appear

Wine	Treated wine %					
	0	5	10	15	20	25
Fino	3	3	5	>7	>7	>7
Medium	5	6	>7	>7	>7	>7
Cream	>7	>7	>7	>7	>7	>7

Influence on the oxidative stability of the fino wine Tests of oxidative stability of mixtures in different proportions of treated and untreated fino wines were carried out, the results being presented in Table 2. As can be observed, as the proportion of treated wine in the mixtures increased, the absorbance increments during the oxidation tests decreased, being in the 100% treated wine 1/3 or 1/2 of the control at 420 nm and 470 nm respectively. This is because treated wines have smaller concentrations of phenolic compounds and catalytic metals, mainly Fe and Cu, and smaller pH values, factors which decrease the wine oxidation rate [32, 33].

Proton exchange and cold treatment experiments on an industrial scale

The results are in general similar to those obtained on a laboratory scale, although it should be noted that only the load phase was used.

Determination of the optimum proportion of treated wine. To determine the proportion of treated wine that should be mixed with untreated wine to obtain a stable wine for at least 7 days at –6 °C, samples with mixtures of different proportions were prepared, and the test of tartrate stability was carried out (Table 3). As can be observed, for the fino wine a mixture of 15% of treated wine was required, while the medium wine required a mixture of 10%, and the cream would be stable without any treated wine. Despite that, for this wine a mixture of 10% was used as a precaution.

Effect on the sensorial characteristics of wines No large differences between the sensorial characteristics of the two stabilization techniques were observed, as can be seen in the sums of the scores and preferences of the wines treated by the two techniques (Table 4).

Comparison of proton exchange and cold treatment No significant differences in the effect on pH of the two tech-

Table 2 Absorbance increases during the accelerated oxidation tests in mixtures of treated and untreated wine. Values in absorbance units

λ nm	Mixture composition (% treated wine)								
	0	5	10	15	20	30	40	50	100
420	0.025	0.022	0.020	0.018	0.017	0.015	0.011	0.009	0.007
470	0.019	0.019	0.018	0.018	0.018	0.017	0.015	0.014	0.009

Table 4 Results of the tastes of the wines stabilized by proton exchange and cold treatment. Values of scores from 0 (minimum) to 5 (maximum) *PE* Proton exchange, *CT* cold treatment

Wine	Sight		Smell		Taste		Total		Preferences		
	PE	CT	PE	CT	PE	CT	PE	CT	PE	CT	Equal
Fino	3.47	4.53	3.48	4.28	3.37	3.81	10.32	12.62	1	4	0
Medium	4.26	3.86	3.9	3.1	3.77	3.89	11.93	10.85	4	0	1
Cream	4.07	4.07	3.82	3.82	4.29	4.17	12.18	12.06	2	1	2
Total	11.8	12.46	11.2	11.2	11.43	11.87	34.43	35.53	7	5	3

Table 5 Composition of the controls, proton exchange and cold treated wines for fino wines. *C* Control, PE proton exchange, CT cold treatment, H_2T tartaric acid

Wine	pH	Conductivity µS/cm	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Fe mg/l	H_2T g/l	A_{420}
C	3.12	1816	32	800	71	60	3.3	3.05	0.133
PE	2.97	2038	28	689	60	51	3.0	3.05	0.127
CT	3.01	1596	34	580	71	60	3.3	1.98	0.119

Table 6 Composition of the controls, proton exchange and cold treated wines for medium wines. C Control, PE proton exchange, CT cold treatment, H_2T tartaric acid

Wine	pH	Conductivity µS/cm	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Fe mg/l	H_2T g/l	A_{420}
C	3.15	1829	56	940	80	77	3.0	2.90	0.438
PE	3.05	2071	52	851	72	69	2.7	2.90	0.431
CT	3.05	1689	70	740	96	80	3.0	2.20	0.398

Table 7 Composition of the controls, proton exchange and cold treated wines for cream wines. C Control, PE proton exchange, CT cold treatment, H_2T tartaric acid

Wine	pH	Conductivity µS/cm	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Fe mg/l	H_2T g/l	A_{420}
C	3.34	1790	60	900	76	75	3.3	1.95	0.457
PE	3.25	1933	54	815	68	68	3.0	1.95	0.454
CT	3.30	1720	73	860	84	75	3.3	1.81	0.442

niques were observed, because the maximum observed difference was 0.05 units (Table 5, Table 6, Table 7). An increase in the conductivity of the proton exchange-treated wines due to their slightly larger content in H^+ ions was observed, and also a decrease in the cold-treated wines due to their lower KHT content. The decreases in the potassium concentrations in the proton exchange treatments correlated to the percentage of treated wine mixed, while in the cold treatment, the reduction depended on the wine nature, and was of very small magnitude in the cream wine. Smaller concentrations of the ions Na^+, Ca^{+2}, Mg^{+2} and $Fe^{+2/+3}$ in proton exchange-treated wines were observed, which is especially interesting in Ca and Fe, because of their effects on wine stability. Furthermore, an increase in the concentrations of the Ca^{+2} and Na^+ ions during cold treatment was observed, due to cession by the filtration earths. Lastly, it should be remarked that proton exchange had no effect on the tartaric acid content and that cold treatment produced a larger reduction of the wine's colour intensity, due to the wine's colouring matter insolubilization at low temperature, this being especially noticeable in medium and cream wines.

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