USE OF ION EXCHANGE RESINS FOR TARTRATE WINE STABILIZATION

UTILISATION DE RÉSINES ÉCHANGEUSES D'IONS POUR LA STABILISATION TARTRIQUE DES VINS

Helena MIRA[1], Patrícia LEITE[1,2,3],
J. M. RICARDO-DA-SILVA[2*] and A. S. CURVELO-GARCIA[3]

1: Escola Superior Agrária de Santarém, Apartado 310, 2001-904 Santarém, Portugal
2: Universidade Técnica de Lisboa, Instituto Superior de Agronomia, Laboratório Ferreira Lapa (Sector de Enologia), Tapada da Ajuda, 1349-017 Lisboa Codex, Portugal
3: INIAP, Estação Vitivinícola Nacional, Quinta da Almoínha, 2565-191 Dois Portos, Portugal

Abstract: The application of the cation exchange and double cation-anion exchange resins, regarding the wine tartrate stabilization, without previous treatment of wine by cold has been studied as well as their influence in phenolic, mineral and organic acid composition. The R1 resin was used in Mg^{2+}, Na^{+} and H^{+} form, the R2 resin was always used in H^{+} form, and the R3 was used in OH- form. The eluted wine was assembled with untreated wine to obtain stable wine. The R2 resin showed to be more efficient to enhance the tartrate stabilization than R1 in Mg^{2+} form; however in H^{+} form, the behaviour of both resins was quite similar. The tartrate stabilization results to double cation anion exchange were similar to the results obtained with cation exchange.

Résumé : L'utilisation de résines échangeuses d'ions pour la stabilisation tartrique des vins, sans préalable traitement par le froid, a été comparée avec le traditionnel traitement par le froid. Deux résines échangeuses de cations (R1 et R2) et une échangeuse d'anions (R3) ont été utilisées pour la stabilisation tartrique de vins portugais de la région Ribatejo (Portugal). La résine R1 a été utilisée sous la forme de magnésium, sodium et hydrogène, la résine R2 a toujours été utilisée sous la forme d'hydrogène, tandis que la résine R3 a été préparée sous forme OH^{-}. On a étudié aussi l'influence de l'échange cationique et le double échange cationique-anionique sur la composition phénolique, métallique et en acides organiques des vins.
Initialement, l'étude a comparé différentes solutions de régénération, en ce qui concerne leur influence sur la composition des vins. Si les résines sont régénérées en cycle acide, les cations K^{+} et Ca^{2+} du vin sont replacées par les cations H^{+} avec diminution du pH et augmentation de l'acidité totale. Le vin traité avec la résine R1 sous forme sodium a présenté un grand enrichissement du vin en ce cation. La résine R1 en forme magnésium a montré une affinité plus faible pour le potassium quand on compare avec la même résine sous la forme sodium ou hydrogène, la résine R2 a présenté une affinité similaire à la résine R1-H. La couleur et les composés phénoliques ont diminué dans la phase initiale de passage du vin sur la colonne de résine, avec une accentuation plus marquée dans le double échange.
Après le traitement par les résines échangeuses d'ions, le vin est assemblé avec un certain pourcentage de vin non traité pour obtenir un vin stable. On a fait des assemblages de 5 %, 10 %, 15 % et 25 % de vin traité, le vin témoin (0 %) et le vin après passage total par la résine (100 %) ont été aussi analysés. La résine R2 a présenté une plus grande efficacité pour la stabilisation tartrique que la résine R1 sous forme Mg^{2+}; toutefois la résine R1 sous forme H^{+} est aussi efficace que la résine R2. Le double échange cation-anion n'a pas présenté des résultats plus intéressants que l'échange cationique seul.
Les vins résultants de l'assemblage ont présenté une légère diminution des composés phénoliques, plus importante dans le double échange, due à la rétention dans la structure des deux résines. Le groupe des anthocyanines monoglucosides a montré une plus grande réduction qui les autres groupes, suite à l'utilisation des résines.
Les dégustateurs n'ont pas trouvé de différences significatives entre le vin témoin et les vins traités avec les résines échangeuses de cations.
La technologie des résines échangeuses de cations, avec les résines en cycle acide est un procédé intéressant et alternatif pour la stabilisation tartrique des vins en respectant les limitations imposées par le Code International Œnologique (OIV).

Keywords : tartrate stabilization, cation exchanger, anion exchanger, wine
Mots clés : stabilisation tartrique, résines échangeuses d'ions, vin

*Corresponding author:jricardosil@isa.utl.pt

J. Int. Sci. Vigne Vin, 2006, **40**, n°4, 223-246
©Vigne et Vin Publications Internationales (Bordeaux, France)

INTRODUCTION

The tartrate precipitation in wines is one of the main oenological problems. This natural phenomenon occurs during winemaking and can be observed some months after bottling in untreated wine, according to its evolution. The occurrence of tartrate salt crystals (potassium hydrogen tartrate - KHT and calcium tartrate - CaT) in bottles, with dramatic consequences in the final aspect of the wine, makes tartrate wine stabilization imperative before bottling. Preventive solutions of tartrate precipitation range from physic and chemical treatments to subtractive and additive processes, like cold stabilization (BLOUIN *et al.*, 1979; BURNETT, 1982; SERRANO *et al.*, 1983; MAUJEAN, 1994; MINGUEZ and HERNÁNDEZ, 1998), electrodialysis (ESCUDIER *et al.*, 1985; MOUTOUNET *et al.*, 1997; CAMEIRA-DOS-SANTOS *et al.*, 2000), ion-exchange (AUSTERWEIL, 1953, 1955; DAL CIN, 1984; RANKINE, 1985; MOURGUES, 1993; BENITEZ *et al.*, 2002a), and using protective colloids like yeast mannoproteins (LUBBERS *et al.*, 1993; MOINE-LEDOUX *et al.*, 1997; FEUILLAT and CHARPENTIER, 1998; MOINE-LEDOUX and DUBOURDIEU, 2002a, b) or metatartric acid (WUCHERPFENNIG, 1973; COLAGRANDE, 2002).

Since the middle of last century, the ion exchange technology has been used for tartrate wine stabilization, wine acidification and elimination of metals such as iron, copper and lead (AUSTERWEIL, 1953, 1955; IONESCU, 1969; DAL CIN, 1984; RANKINE, 1985; BONORDEN *et al.*, 1986; LEE, 1991; MOURGUES, 1993; WEINAND and DEDARDEL, 1994; HERNÁNDEZ and MÍNGUEZ, 1997; PALACIOS *et al.*, 2001a, b; WALKER *et al.*, 2002; BENITEZ *et al.*, 2002a, b).

According to their polar groups, ion exchange resins are categorised as strong and weak acid cation exchangers or strong and weak anion exchangers. The active group of cation exchange resins is usually sulphonic-acid (-SO_3H), or a carboxylic acid (CAPUTI, 1994; OIV, 1995). The active radical of anion exchangers is a quaternary ammonium or tertiary amine salt.

RANKINE (1985) and MOURGUES (1993) reported that the wine can be stabilized by ion exchange in three different ways: a) by replacing potassium and calcium with cation of the cation exchange resin; b) by replacing the tartrate anion with hydroxyl or other anion in an anion exchange resin and c) by replacing potassium and calcium, and tartrate, by hydrogen and hydroxyl in a cation and anion exchange resins, exchanging the potassium hydrogen tartrate and the calcium tartrate for water.

The cation exchangers in sodium, magnesium and hydrogen forms may be used to remove the K^+ and Ca^{2+} from the wine (RIBÉREAU-GAYON *et al.*, 1977; RANKINE, 1985; MOURGUES, 1993). In the past, the most common was the use of the cation resins in sodium form (RIBÉREAU-GAYON and PEYNAUD, 1966; TAMBORINI and MAGRO, 1970; RANKINE, 1985). Nevertheless, their use has decreased greatly because the wine stayed much enriched in sodium content. If the cation resin is in hydrogen form, the exchange of cations of the wine by H^+ ions of the resin will originate a very important decrease in pH. To avoid the considerable decrease in the wine pH after treatment, MOURGUES (1993) suggested treating only one fraction of the wine, or using a resin in the mixed forms. In order to avoid a large acidification or an excessive increase in sodium content, we can also use the resin in the magnesium form. Another possibility to prevent the tartrate wine precipitation and minimize the decrease of the wine pH is, in fact, a double cation-anion exchange, however this process could be very drastic, and involves excessive, although temporary, important variations in the pH of the wine (RIBÉREAU-GAYON *et al.*, 1977). Nevertheless, the anion exchanger can have negative effects in the physicochemical composition and sensory characteristics of the wine (BONORDEN *et al.*, 1986; RIBÉREAU-GAYON *et al.*, 1998).

Although the use of the cation and anion exchangers has been authorized in some countries as the United States and Australia; in Europe, the use of the ion exchange resin is only accepted by the Office International de la Vigne et du Vin (OIV) for tartrate stabilization with cation exchangers in acid cycle (OIV, 1995).

The prescriptions of OIV (1998) for tartrate stabilization by treatment with cation exchangers are the following: the treatment must be limited to the elimination of the excess cations, the wine will be initially cold treated and only the minimum fraction of wine necessary for obtaining stability will be treated with cation exchangers; the treatment will be performed using cation exchange resins regenerated in the acid cycle; the whole process will be placed under the responsibility of an enologist or a specialist technician; the resins shall comply with the prescriptions of the International Oenological Codex and shall not lead to excessive modifications of the physicochemical composition and sensory characteristics of the wine.

The limitations for the treatment using cation exchange resin reported by OIV (1995) are the subsequent: the treatment does not alter the character of the wine; does not reduce the colour of the wine to less than the one normally contained in such wines; it does not reduce the metallic cation concentration in the wine to less than 300 mg/L; it does not reduce the pH of the wine to less than 3.0; and the pH reducing does not exceed 0.3 unit of pH; the resin

©Vigne et Vin Publications Internationales (Bordeaux, France)

does not impart to the wine any substances or characteristics which do not normally exist in the wine.

When using ion exchange resins for wine tartaric stabilization purposes, enologists usually perform previous slight cold treatment, as also recommended by OIV (OIV, 1998). So, the aim of this study was the use of the cation exchange and double cation-anion exchange, regarding tartrate wine stabilization, nevertheless without previous cold treatment; and it compares its results with those of the wine submitted only to cold treatment. The effects of this technology in some oenological characteristics of the wine, as the phenolic, mineral and organic acid composition were evaluated. Also, we have studied the influence of the different operational conditions (type of resin and different regenerating solutions) of the ion exchange resins for tartrate wine stabilization, in some oenological characteristics of wines.

MATERIAL AND METHODS

I - WINES

The white wines used in this study were prepared using grapes of Fernão Pires vine variety (*Vitis vinifera* L.) and the red wines using grapes of the Castelão vine variety (*Vitis vinifera* L.). The grapes were harvested in 2001 (white wine and red wine A) and 2002 (white wine and red wine B) at the Ribatejo region (Portugal). The wines have been selected by their degree of tartaric instability, determined with a Boulton test (BOULTON, 1982) modified by VIALATTE (1984). The alcohol content (%, v/v) of the wines was the following: white wine A (11.9), white wine B (11.3), red wine A (12.8) and red wine B (11.3).

II - ION EXCHANGE RESINS

Two strong cation exchange resins were used, R1 (Amberlite SR-1L Na) and R2 (Amberlite FPC-23 H) (Rohm and Haas), both are constituted by a matrix of polystyrene reticulate with divinylbenzene, and with sulfonic functional groups. R1 is a gel type while R2 is a macroporous resin, with a high percentage of divinylbenzene. One anion exchanger was used, R3 (Amberlite IRA-410 Cl), which is a strong basic resin type II, with polystyrene matrix.

III - ION EXCHANGE SYSTEM AND EXPERIMENTS

The experiments have been carried out using appropriate resin columns with of 20 cm or 50 cm height and 2.5 cm internal diameter (Bio-Rad) and with a reservoir at the top. A peristaltic pump Masterflex, model 7550-62 (Cole-Parmer Instrument Company, Chicago-Illinois, USA) was used to control the flow in the columns with food-grade tubing (Norpene food -A60F, type 14).

The regeneration of the R1 resin was carried out with three different solutions: NaCl (30 % p/v) (R1-Na), $MgCl_2$ (15 % p/v) (R1-Mg) and HCl (30 % v/v) (R1-H), the R2 resin was regenerated with HCl solution (30 % v/v) and the R3 resin with NaOH solution (30 % p/v). The regeneration phase of the cation exchange resins was carried out with percolation of ten bedvolumes (liquid volume/resin volume) of the solution through the exchangers' column. The anion resin was regenerated in immersion using ten bedvolumes of NaOH solution, the mixture was agitated during 75 minutes in an automatic agitator.

1) Experiments with cation exchangers

To evaluate the influence of the cation exchangers in the wine composition and the breakthrough point for the cations we are studying (potassium, calcium, sodium, magnesium, iron and copper), the wine previously filtered, passed through a column of polymerized resin, and different samples of the effluent were collected at regular intervals. In these fractions, some oenological parameters were measured.

In the second part, the exchanged wine was mixed in different proportions (5 %, 10 %, 15 % and 25 %) with the untreated wine. The control wine (represented at 0 %), and the eluted wine (represented at 100 %) were also analysed. In each lot, we have performed the analytical determinations. The control wines were subjected to a cold treatment; thus, the wines were refrigerated at 0 ºC (the lowest temperature available in our experimental conditions) and kept at this temperature for 4 weeks. The assays were performed in duplicate.

2) Experiments with anion exchanger

To evaluate the effect of the anion resin in the main wine characteristics, different samples of eluted wine were collected at regular intervals and some parameters were measured, as in the cation experiments.

3) Experiments with cation and anion exchangers

As in the previous experiments, the wine passed through the resins, first in cation resin and after that in anion resin; different samples of the effluent wine were collected at regular intervals, and some oenological parameters were measured.

In the second part, the exchanged wine passed previously through a cation resin and next an anion resin was mixed in different proportions (5 %, 10 %, 15 % and 25 %) with the original wine. The control wine and the eluted wine (represented by 0 % and 100 %, respectively) were also analysed. The assays were performed in duplicate.

©Vigne et Vin Publications Internationales (Bordeaux, France)

IV - MINERAL COMPOSITION ANALYSIS

The concentration of cations (potassium, calcium, sodium, magnesium, iron and copper) was carried out by flame atomic absorption spectrophotometry (FAAS) using a Varian Spectra 10/20 (Victoria, Australia), according to the official methods of OIV (OIV, 1990). Chlorides content was determined by potentiometric method (OIV, 1990) using a PHM 82 Standard pH meter (Radiometer Analytical, Lyon, France).

V - COLOUR AND PHENOLIC COMPOUNDS EVALUATION

The total content of the phenolic compounds was measured by the absorbance at 280 nm (RIBÉREAU-GAYON, 1970); tonality is defined as the ratio (A_{420} nm/A_{520} nm) and colour intensity as the sum (A_{420} nm+A_{520} nm+A_{620} nm). For the white wine, to measure the wine colour intensity it was used the absorbance at 420 nm. Colour measurements of the wines were also performed according to the CIELAB 76 method (McLAREN, 1980). Spectral readings-transmittance every 10 nm over visible spectrum, 380-770 nm were performed with a UV4 Unican Visible Spectrometry (Cambridge, UK), using quartz cells of 1-mm (red wine) or 10-mm (white wine) path length. The software Chroma 2.0 colour measurement was used to directly calculate the CIELAB coordinates. L*, a* and b* values describe a tree-dimensional colour space. The vertical axis L* is a measure of lightness, from completely opaque (0) to completely transparent (100), whereas on the hue-circle a* is a measure of redness (or -a* of greenness), and b* of yellowness (or -b* of blueness).

To red wine, the total pigments were estimated using the method of SOMERS and EVANS (1977); polymeric pigment index was determined by a method proposed by GLORIES (1978) and total anthocyanins evaluated according to the method of RIBÉREAU-GAYON and STONESTREET (1965). The data of each measurement are the average of duplicate samples.

VI - ACID COMPOSITION ANALYSIS

Organic acids (tartaric, malic, citric, lactic and shikimic acid) were analysed by high performance liquid chromatography using a method described by TUSSEAU and BENOIT (1986a, b). Two columns with reverse phase Lichrospher 100 RP 8 (Merck, Darmastadt, Germany) (particle size 5 µm, 250 x 4 mm) were used. Detection was made with a UVIS 206 PHD (KONIK Instruments, Barcelona, Spain) set at 210 nm, and the peak areas were determined with Konikchrom 5.2 software.

pH, titrable and volatile acidity were determined by Fourier Transform Infrared Spectrometry - FTIR (WineScan FT120, Foss, Slangerupgade, Denmark)

Table I - Evolution of cations and chloride anion content in the eluted white and red wine A, using R1 resin in Na^+ form (R1-Na) or in Mg2+ form (R1-Mg)
Evolution de la concentration des cations et d'anion chlorure dans les vins blanc et rouge A, après l'utilisation de la résine R1 sous forme Na^+ (R1-Na) ou sous forme Mg^{2+} (R1-Mg)

		R1-Na						R1-Mg					
	bv	K (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	Cu (mg/L)	Fe (mg/L)	Cl (mg/L)	K (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	Cu (mg/L)	Fe (mg/L)	Cl (mg/L)
White Wine A	**T**	650	73	26	75	0.1	0.9	20	651	74	27	75	0.1	1.1	21
	8	**1**	**nd**	**1014**	nd	nd	0.6	20	**198**	**10**	6	**345**	0.1	0.7	19
	20	nd	nd	956	nd	nd	0.5	19	268	5	22	315	0.1	0.9	21
	30	nd	nd	893	nd	nd	0.5	21	516	nd	25	230	0.1	0.8	19
	40	nd	nd	875	nd	nd	0.5	19	624	2	27	198	0.1	0.9	20
	50	17	2	822	nd	nd	0.5	20	656	1	28	188	0.1	0.7	18
	60	528	1	438	nd	nd	0.5	20	648	nd	30	188	0.1	0.8	18
Red Wine A	**T**	1162	87	14	64	0.1	4.8	35	1150	87	15	65	0.1	4.8	34
	8	**nd**	**nd**	**1174**	nd	nd	2.1	34	**254**	**13**	11	**470**	0.1	3.6	33
	20	1	nd	1148	nd	nd	2.4	33	550	10	23	368	0.1	3.4	34
	30	3	nd	1120	nd	nd	2.4	33	934	5	24	243	0.1	2.7	33
	40	76	1	1050	nd	nd	2.4	33	1170	5	26	200	0.1	2.8	33
	50	1322	2	262	nd	nd	2.4	34	1230	3	25	175	0.1	1.3	34
	60	1889	1	40	nd	nd	2.3	33	1205	8	25	165	0.1	1.4	34

Legend: nd - not detected; R1-Na cation exchange resin in sodium form; R1-Mg cation exchange resin in magnesium form; bv- bedvolumes; resin volume = 50 mL; flow = 2.7 ml.min^{-1}

©Vigne et Vin Publications Internationales (Bordeaux, France)

(MOREIRA *et al.*, 2002a, b), and the wine pH was also determined by a potentiometric method (OIV, 1990).

VII - WINE TARTRATE STABILITY EVALUATION

Tartrate stability evaluation was done using two methods: the mini-contact method, which was reported by BOULTON (1982) and modified by VIALATTE (1984) and the determination of the temperature of saturation in wines (WURDIG *et al.*, 1982; MAUJEAN *et al.*, 1985) optimised by CAMEIRA-DOS-SANTOS *et al.* (2002). By the mini-contact method, the wine stability assessment is based on the difference between initial conductivity (Ci) and final conductivity (Cf). Generally, if such difference is less than 5 % of the original value, the wine is stable; otherwise the wine is instable. In what concerns the saturation temperature (Tsat), according to MAUJEAN *et al.* (1985) white wines are considered stable if Tsat is below 12 ºC-13 ºC, what means there isn't the risk of tartrate crystals precipitation.

The conductivimeter used to perform the Boulton method was a 220 model, Denver Instrument Company (Colorado, USA). The determination of the temperature of saturation requires the measurement of the wine conductivity by increasing the temperature at a constant rate; a Crison micro CM 2201 conductivity meter (Barcelona, Spain) was used to measure the values of conductivity and temperature. These values were registered by a personal computer by means of RS232 port using acquisition data software written by CAMEIRA-DOS-SANTOS *et al.* (2002). The wine was cooled to near 0 ºC and then heated at predetermined heating rate up to 30 ºC. The same procedure was done with the wine containing 4 g/L KHT crystals. The heating rate was controlled by a programmable bath Huber Polystat K6 (Offenburg, Germany). The saturation temperature is determined by the intersection of the curves of conductivity versus temperature for both wines, with and without addition of crystals.

VIII - SENSORY EVALUATION

The six expert panellists were members of « Comissão Vitivinícola Regional do Ribatejo (CVRR) », they were trained and had previous experience. We asked to the panellists the differences between the control wine and each sample of the assembled wine, randomized before presentation. The attributes of the wine, corresponding to the visual, nose and taste senses, as well as the global appreciation of each wine were carried out. Only the wines A, treated with cation exchange resins, were submitted to sensorial evaluation, owing the availability of the panel test.

IX - STATISTICAL ANALYSIS

The factorial treatment design contained two factors: ion-exchange resins (R1 and R2, or R1+R3 and R2+R3) and a proportion of the treated wine (0 %, 5 %, 10 %, 15 %, 25 % and 100 %). The data were analyzed by Analysis of Variance using SPSS 12.0 for Windows. The treatment means were separated by Scheffée test at the 5 % significance level.

RESULTS AND DISCUSSION

I - EFFECT OF THE TYPE OF RESIN AND REGENERATING SOLUTION IN SOME WINE PARAMETERS

1) Cation exchange resins experiments

a) Influence of the mineral composition

The resins showed a general behavior that can be observed in two differentiated phases. During the first one, named the « load phase », important exchange reactions took place among the cations presented in the wine and the cation fixed into the resin. In the « unload phase », there are not initial cations fixed into the resin available to be transferred from the resin to the wine. At this moment, new exchange reactions occur among the dissolved wine cations with higher affinity and the fixed cations with less affinity. In this phase, part of the low-affinity fixed cations returns to the wine.

The results for R1 resin regenerated with different solutions are presented in tables I and II. The wines subjected to treatment with the R1 resin in sodium or hydrogen form showed a large decrease in the potassium, calcium and magnesium content, demonstrating the good affinity of the resin to those cations. However, the wine treated with R1-Na (table I) revealed a wide release in sodium from the structure of the resin, reaching a high concentration in exceeding sodium (> 1g/L); this evidence is not suitable once the maxim limit of the exceeding sodium content established by OIV (1990) is 60 mg/L (express in NaCl), and for USA the limit is 200 mg/L. The increase in sodium content was more important in the red wine than in the white wine, due to a greater amount of cations in the red wine. Later, the concentration of the potassium started to increase in the wine, indicating that it was reached the equilibrium between the sodium in the resin and the cations presented in the wine; the cation exchange continued with the release of the potassium cation. The breakthrough point of the potassium was verified around 50 bedvolumes for white wine and 40 bedvolumes for red wine; during all the process we didn't find the breakthrough point to calcium, indicative of good affinity to this divalent cation. The R1-Na resin showed some affinity to iron.

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table II - Evolution of cations and chloride anion content in the eluted white and red wine, using R1 and R2 resin in H^+ form

Evolution de la concentration des cations et d'anion chlorure dans les vins blanc et rouge, après l'utilisation des résines R1 et R2 sous forme H^+

		bv	K (mg/L)	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	Cu (mg/L)	Fe (mg/L)	Cl (mg/L)	pH
R1-H	White Wine (B)	**0**	581	77	24	75	0.2	1.3	31	2.96
		10	**nd**	**nd**	nd	nd	nd	0.1	32	**1.82**
		20	nd	nd	nd	nd	nd	0.1	30	1.77
		30	nd	nd	nd	nd	nd	0.2	31	1.76
		40	nd	nd	nd	nd	nd	0.2	31	1.96
		50	nd	nd	nd	nd	0.1	0.3	32	1.91
		60	**125**	nd	47	nd	0.3	0.3	32	**2.48**
	Red Wine (B)	**0**	961	59	21	98	0.1	3.5	34	3.37
		10	**nd**	**3**	1	nd	nd	0.3	36	**1.79**
		20	nd	5	1	nd	nd	0.3	35	1.77
		30	nd	6	1	nd	nd	0.3	35	1.80
		40	nd	5	5	nd	0.1	0.4	35	1.84
		50	**534**	7	104	nd	0.1	1.1	34	**2.69**
		60	1548	6	38	nd	0.1	1.5	34	3.41
R2-H	White Wine (A)	**0**	654	73	27	75	0.1	0.9	19	2.95
		10	**nd**	**2**	nd	nd	nd	0.1	20	**1.78**
		20	nd	2	nd	nd	nd	0.1	22	1.78
		30	nd	1	nd	nd	nd	0.1	19	1.78
		40	nd	3	nd	nd	nd	0.1	19	1.80
		50	nd	1	nd	nd	nd	0.3	22	2.00
		60	**95**	6	61	nd	nd	0.4	21	**2.49**
	Red Wine (A)	**0**	1156	87	14	64	0.1	4.8	35	3.41
		10	**nd**	**nd**	nd	nd	0.1	0.4	33	**1.79**
		20	1	nd	nd	nd	0.0	0.6	34	1.78
		30	nd	1	nd	nd	0.1	1.0	32	1.79
		40	3	2	1	nd	0.1	2.1	31	1.99
		50	**979**	nd	73	nd	0.1	2.7	34	**3.10**
		60	1788	1	31	nd	0.1	2.9	33	3.46

Legend: nd - not detected; bv - bedvolumes; resin volume = 50 mL; flow = 6 $ml.min^{-1}$

The R1-Mg resin (table I) showed a smaller affinity to potassium than R1-Na resin, whose breakthrough point to potassium was verified at 16 bedvolumes both to the white and the red wine. These results were in accord with WEINAND and DEDARDEL (1994) who reported that the affinity of exchange increases with the valence of the exchanger ion; the exchanger has more difficulty in replacing the magnesium for potassium; confirming this is the good affinity verified to Ca^{2+}. A great release of magnesium into wine was observed. Nevertheless, this cation doesn't cause any health problems, and doesn't have any influence in sensory characteristics and in wine quality (RIBÉREAU-GAYON *et al.*, 1977).

The R1-H resin (table II) showed a good affinity to potassium, sodium, calcium and magnesium. The variation of the concentration of potassium and sodium during the process is similar; the breakthrough point of these cations has occurred around 50 bedvolumes for white wine and 40 bedvolumes for red wine. The resin had some affinity to iron. The samples showed a considerable decrease in pH to values less than 2.0 pH-values (figure 1) and remained constant during the load phase. This confirms the cation exchange between H^+ in the resin and the cations presented in the wine; later, when the ionic equilibrium was reached in the resin, the rate of the H^+ decreased and the pH of the eluted wine picked up gradually to the pH of the control wine, what is consistent with the previous results of MOURGUES (1993). The increase in titrable acidity is related to the increase of the H^+ content; confirming the data obtained by WALKER *et al.* (2002). The variation of the pH in the eluted wines treated with resins in sodium or magnesium form was negligible.

The different forms of the R1 resin showed high affinity to calcium as it is a divalent cation.

Using the R2 resin (table II), the results showed a good affinity to potassium, calcium, sodium and magnesium, similar behaviour observed to R1-H mentioned above. The breakthrough point to potassium occurred around 60 bedvolumes to white wine and 50 bedvolumes to red wine.

Both resins, R1 and R2, have shown small affinity to copper, probably due to the small content of this metal presented by our wines. Some authors (PALACIOS *et al.*, 2001a; BENITEZ *et al.*, 2002b) using other functional resins have shown good affinity to copper, however their wines had higher copper levels.

b) Influence on colour and phenolic composition

In general, for white wine (figure 2) it was observed an initial quick decrease in the total phenol index and some increase in the absorbance at 420 nm during the

©Vigne et Vin Publications Internationales (Bordeaux, France)

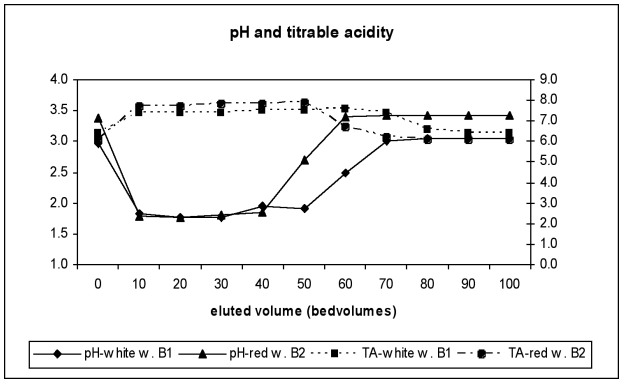


Figure 1 - Evolution of pH and titrable acidity (TA) in treated wines B of the cation exchange R1-H

Évolution du pH et de l'acidité totale des vins B, après passage sur la résine échangeuse de cations R1-H

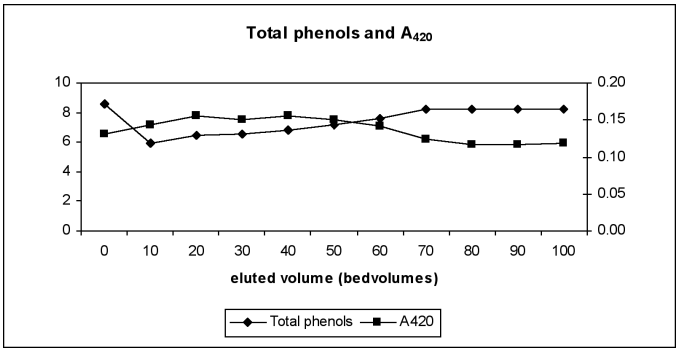


Figure 2 - Evolution of the total phenol index and absorbance at 420 in treated white wine B of the cation exchange R1-H

Évolution de l'indice de phénols totaux et de la A420 du vin blanc B après passage sur la résine échangeuse de cations R1-H

Table III - Characteristics of eluted white wine B using double exchange with R1 and R3 resins

Caractéristiques du vin blanc B après passage sur les résines échangeuses R1 et R3

bedvolumes	0	10	20	40	60	80	100
Total Phenol Index	7.4	**0.8**	2.6	2.9	3.6	3.9	4.4
A_{420} (ua)	0.113	0.013	0.029	0.028	0.031	0.031	0.037
L*	97.7	100.1	99.6	99.5	99.3	99.7	99.5
a*	-0.34	-0.10	-0.23	-0.35	-0.49	-0.58	-0.58
b*	6.66	0.79	1.78	2.12	2.69	2.17	2.65
Potassium (mg/L)	574	**nd**	nd	nd	nd	843	818
Calcium (mg/L)	78	**15**	3	nd	nd	nd	nd
Sodium (mg/L)	24	1	nd	nd	2	41	27
Magnesium (mg/L)	77	15	24	1	1	1	3
Copper (mg/L)	0.2	nd	0.1	0.1	nd	0.1	0.1
Iron (mg/L)	1.3	nd	nd	nd	0.2	0.1	0.1
Chloride (mg/L)	31	na	7	49	88	228	109
pH	3.08	3.18	3.09	2.49	2.57	3.09	3.21
Titrable Acidity (g/L tartaric ac.)	6.3	0.5	2.9	7.7	8.0	6.5	6.3
Tartaric Ac. (g/L)	3.6	**nd**	0.1	3.9	4.0	3.5	3.2
Malic Ac. (g/L)	2.2	**0.1**	1.1	2.3	2.1	1.9	2.0
Shikimic Ac. (mg/L)	37	**8**	44	34	30	33	33
Lactic Ac. (g/L)	1.4	**nd**	0.6	0.2	0.6	1.0	1.1
Citric Ac. (mg/L)	999	**157**	499	480	590	857	971

Legend: nd - not detected; na - not analysed, R1 - cation exchange resin in H^+ form, R3 - anion exchange resin in OH^- form; resin volume = 50 mL; flow = 6 $ml.min^{-1}$

load phase, followed by a slow increase of the total phenols and a decrease of A420 until it reached similar values to the control wine. Phenolic parameters and chromatic characteristics of the red wine treated with R1-Na and R1-Mg (data not shown) revealed an initial decrease in these parameters in the load phase, comparatively to control wine; followed by a slow increase. Similar evolution was observed to the wine treated with resins in the hydrogen form, although the differences to the control wine were higher. The results of the red wine treated with R1-H and R2-H indicated that it had an initial retention of phenolic compounds in the matrix resin, expressed for the reduction of total phenols index, total anthocyanins content and total pigments colour, confirming later some release of the anthocyanins from the resin matrix (data not shown), although these results didn't have relevant oenological implications.

c) Influence on the organic acid composition

As expected, the cation exchange did not affect the concentration of the organic acids evaluated by HPLC (data not shown). The organic acid content in the white wine A was the following: tartaric acid (3.8 g/L), malic acid (2.6 g/L), shikimic acid (40 mg/L), lactic acid (0.5 g/L) and citric acid (873 mg/L). The organic acid

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table IV - Characteristics of eluted red wine B using double exchange with R1 and R3 resins

Caractéristiques du vin rouge B après passage sur les résines échangeuses R1 et R3

bedvolumes	0	10	20	40	60	80	100
Total Phenol Index	53.9	**30.0**	31.8	39.2	42.2	41.9	43.8
Colour Intensity (ua)	13.23	6.74	8.72	14.97	15.65	10.69	10.65
Tonality (ua)	0.556	0.838	0.573	0.423	0.420	0.564	0.589
L*	64.2	80.5	74.3	62.7	61.1	69.9	69.8
a*	41.10	16.22	31.50	52.38	53.30	36.64	35.16
b*	-2.13	2.14	0.12	0.65	1.44	0.07	0.14
Total anthocyanins (mg/L)	382.2	132.0	129.3	235.4	287.4	279.2	302.7
Polymerized Pigments Index (%)	45	66	62	56	49	51	49
Total pigments colour (ua)	36.60	14.83	16.27	25.07	24.43	24.40	25.50
Potassium (mg/L)	894	**8**	3	nd	269	1313	1261
Calcium (mg/L)	60	**nd**	nd	nd	nd	nd	nd
Sodium (mg/L)	21	1	2	1	35	26	24
Magnesium (mg/L)	101	4	1	1	1	2	2
Copper (mg/L)	0.1	0.1	0.1	nd	0.1	nd	nd
Iron (mg/L)	3.5	0.4	0.2	0.4	0.6	0.4	0.4
Chloride (mg/L)	34	nd	nd	19	135	299	124
pH	3.38	3.18	3.09	2.64	2.73	3.27	3.40
Titrable Acidity (g/L tartaric ac.)	5.4	0.5	3.2	6.9	7.3	5.2	5.3
Tartaric Ac. (g/L)	2.6	**nd**	0.1	1.2	3.5	2.1	2.7
Malic Ac. (g/L)	0.2	**nd**	nd	0.3	0.2	0.2	0.3
Shikimic Ac. (mg/L)	28	**nd**	38	28	27	26	27
Lactic Ac. (g/L)	3.3	**0.1**	3.3	3.6	3.7	3.8	3.4
Citric Ac. (mg/L)	998	**212**	650	1063	932	975	891

Legend: nd - not detected; R1 - cation exchange resin in H+ form, R3 - anion exchange resin in OH- form; resin volume = 50 mL; flow = 6 ml.min^{-1}

composition of the red wine A was the subsequent: tartaric acid (2.3 g/L), malic acid (0.4 g/L), shikimic acid (35 mg/L), lactic acid (3.5 g/L) and citric acid (947 mg/L). The values obtained for organic acids analysis of the control white and red wines B were presented in tables VII and XIII, respectively.

2) Anion exchange resin experiments

The anion exchangers are commonly used in association with the cation exchangers. Nevertheless, we have studied the influence of the anion exchange in some wine characteristics. The white and red wines showed significant variations in the colour characteristics from the beginning of the load phase. Concerning the white wine, the total phenol index and the absorbance at 420 nm presented lower values when compared with the control wine (data not shown). The lightness increased for values next to 100 % in the first samples; these results were in accordance with the visual observation in which the eluted wine showed totally transparent, due to a great retention of the wine constituents in the matrix resin. In the initial phase of treatment, the red wine presented a decrease in the content of the phenolic compounds as well as in a total pigments colour and anthocyanin content comparatively to the control wine, probably due to adsorption of phenolic compounds in the matrix resin, which contribute to a colour modification of the resin (visually identified). A large increase (from 50 % to 82 % in the first 10 bv) of the polymerized pigment index can be related with the possible retention of the monomeric pigments once the total pigments decreased quickly.

It was verified a large increase (from 3.42 to 11.44 in the first 10 bv) in the wine pH, great in the red wine, this fact is consequence of ion exchange between OH^- in the resin and the anions presented in the wine. It was also observed a wide release of Cl^- anion (from 32 mg/L to a maximum of 381 mg/L at the 35 bv), during the regeneration of the resin, the dissolved OH^- in the regeneration solution were exchanged with the Cl^- anions in the resin, but possibly some Cl^- anions remained in the matrix resin, which later were exchanged with the wine anions.

The R3 resin has shown some affinity to organic acids, mainly to tartaric acid; despite that, the breakthrough point to tartaric acid was verified at around 20 bedvolumes and slightly earlier to the other organic acids. As expected, the anion resin doesn't be influence the cations content (data not shown).

3) Cation and anion exchange resins experiments

The two resins, in a sequential use, have presented a similar behaviour; the wide differences between control and eluted wine were show in the first collected sample,

©Vigne et Vin Publications Internationales (Bordeaux, France)

nevertheless the values recovered progressively to the control wine values.

a) Influence on the mineral composition

As it can be observed in table III, the white wine treated with R1+R3 resins presented initially an important decrease in the concentration of all cations. The breakthrough point to potassium was around 60 bedvolumes, slightly upper than the verified in the previous experiment. The sodium had a similar behaviour as potassium. During the unload phase the concentrations of potassium and sodium were higher than the ones shown by the control. The concentrations of the calcium, magnesium and iron were low and constant in the eluted wine during the whole experiment, due the good affinity of the resin to these cations. Initially, the chloride anion is partially retained in the anion resin matrix, but at 20 bedvolumes the concentration of chlorides increases significantly, to values greater than the chlorides content of the control wine. This suggests that, in addition to the release of fixed chloride anions, some chlorides which were not exchanged with the OH^- during the operation of the resin regeneration-phase were released in the load phase.

The results for white wine using R2+R3 resins (data not shown) were similar to the observed with R1+R3 resins, but the breakthrough point to potassium occurred at 50 bedvolumes; earlier than in the experiment with R1+R3 resins.

For the red wines, the results observed using the R1+R3 resins or R2+R3 are quite similar. The breakthrough point to potassium was reached at 50 bedvolumes to the wine treated with R1+R3 resins (table IV) and at 40 bedvolumes to the wine treated with R2+R3 (data not shown). Using R1+R3, the sodium had the same behaviour as the potassium, although R2+R3 had showed less capacity to restraint the sodium. The two groups of resins showed a great reduction of calcium and magnesium content. Relatively to Cl^-, a significant retention in the first fractions was verified; being the breakthrough point around 20 bedvolumes, the same as is in the previous experiments.

b) Influence on colour and phenolic composition

The results of the eluted white wine using double exchange with R1+R3 resins are presented in table III, and are similar to those observed using R2+R3 resins (data not shown). As it can be observed, the double exchange presented a great reduction in the phenolic compounds and in the colour characteristics of the wine when compared to the treatment with only one resin. As mentioned, in general, it was observed bigger differences between the first collected samples and the control wine followed by a slow increase until it reached the control wine values. The reduction of the total phenols content and the absorbance values at 420 nm indicating the retention of the phenolic constituents in the resins matrix which influenced the wine colour and increased the wine lightness.

The results of eluted red wines using R1+R3 resins (table IV) and R2+R3 resins (data not shown) were rather similar. The eluted wines showed important reduction in the total phenols, total anthocyanins content and total pigment colour, probably due to a considerable retention of the phenolic constituents of the wine in the two resins matrix. The polymerized pigments index had a sharp increase in the first collected samples and diminished later, however always presenting high values comparatively to control wine, indicating that the ratio of polymerized pigments in the eluted wine increased. The variations of the colour intensity, tonality and chromatic characteristics are related to the retention of the wine constituents in the matrix resins and pH wine.

c) Effect in the organic acid composition

The experiments revealed that the resin had a better affinity to acid tartaric. For white wines, the results indicated that the breakthrough point to tartaric acid occurred at around 20 bedvolumes and slightly earlier than other organic acids. Similar results were observed with the red wine.

d) Tartrate wine stabilization

The process of tartrate wine stabilization must be carried out during the load phase. In this phase, the potassium, calcium and other cations are retained with very good effectiveness. However, if the treatment is prolonged already to the load phase, some cations initially retained by the resin will be released to the wine, mainly monovalent cations, according to the affinity laws. The cycle volume of the process corresponding to the load phase is in general 50 bedvolumes in the white wines and 40 bedvolumes in the red wines.

Both resins demonstrated to be effective in reducing the content of calcium; the wines are that predisposed to Ca^{2+} precipitation can be stabilized with the ion exchange technology which is not entirely possible with cold treatment, as suggested by HERNÁNDEZ and MÍNGUEZ (1997), as this treatment is particularly targeted to potassium cation and tartaric anion of wines.

Given the effectiveness of the potassium and calcium removal, the reduction in pH wine, and losses in phenolic compounds particularly the anthocyanins, is suitable to treat the wine partially and blend it with the rest of the wine.

II - TECHNOLOGICAL ASSAYS WITH WHITE AND RED WINES

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table V - Main effects of cation-exchange resins and different proportions of treated and untreated wine by cation exchange on some white wine A characteristics

Influence des résines échangeuses de cations et des proportions croissantes de vin traité sur les caractéristiques du vin blanc A

Treatment	**Ipt**	**A420** (ua)	**L***	**a***	**b***	**K** (mg/l)	**Ca** (mg/l)	**Na** (mg/l)	**Mg** (mg/l)	**Cu** (mg/l)	**Fe** (mg/l)	**Cl** (mg/l)	**H_2T** (g/l)	**pH**	**TA** (g/l)	**VA** (g/l)
Cation exchange Resins	**	**	ns	**	**	**	*	**	**	ns	ns	ns	ns	**	**	ns
R1-Mg	6.9b	0.101b	98.8a	-0.71c	6.49c	542c	55b	26a	144b	0.1a	0.9a	20a	3.8a	3.10b	7.7a	0.34a
R1-Na	6.6a	0.097a	98.7a	-0.91a	6.27a	460b	54a	165b	58a	0.1a	0.9a	20a	3.8a	3.10b	7.6a	0.34a
R2-H	6.6a	0.097a	98.6a	-0.80b	6.34b	433a	53a	20a	57a	0.1a	0.9a	20a	3.7a	2.92a	8.1b	0.32a
Proportion of treated wine (%)	**	**	ns	**	ns	**	**	ns	ns	ns	ns	ns	ns	**	**	**
0	7.1cd	0.104d	98.6a	-0.99a	6.50c	619e	74f	27a	76a	0.1a	0.9a	20a	3.8a	3.08d	7.7a	0.30a
5	7.1cd	0.102cd	98.6a	-0.93b	6.56d	563d	69e	37a	82a	0.1a	0.8a	20a	3.7a	3.07d	7.7a	0.32a
10	6.9bc	0.102c	99.1a	-0.64d	6.60e	529c	65d	50a	84a	0.1a	0.9a	19a	3.8a	3.07d	7.7a	0.32a
15	6.8bc	0.103c	98.5a	-0.85c	6.55d	520c	61c	58a	86a	0.1a	0.9a	20a	3.7a	3.04c	7.7a	0.31a
25	6.7b	0.098b	98.5a	-0.85c	6.45b	477b	54b	83a	88a	0.1a	0.8a	19a	3.7a	3.02b	7.7a	0.32a
100	5.8a	0.081a	98.7a	-0.59e	5.53a	162a	3a	168a	104a	0.1a	0.8a	20a	3.7a	2.94a	8.1b	0.42b
Interaction	ns	**	ns	**	**	**	**	**	**	ns	ns	ns	ns	**	**	**

Treatment means were separated by Scheffée test at the 5 % significance level. Different letters in the same column indicate statistically significant differences: * ($p \leq 0.05$), ** ($p \leq 0.01$), ns-not significant. R1-Na cation exchange resin in sodium form; R1-Mg cation exchange resin in magnesium form; R2 - cation exchange resin in hydrogen form, resin volume = 50 mL; flow = 2.7 $ml.min^{-1}$

Ipt - Total phenols index; A_{420} - Absorbance at 420 nm; L*, a* and b* - CIELAB cordinates; H_2T - Tartaric Acid; TA - Titrable Acidity; VA - Volatile Acidity

Table VI - Main effects of cation-exchange resins and different proportions of treated and untreated wine by proton exchange on some white wine B characteristics

Influence des résines échangeuses de cations en cycle acide et des proportions croissantes de vin traité sur les caractéristiques du vin blanc B

Treatment	**Ipt**	**A420 (ua)**	**L***	**a***	**b***	**K** (mg/l)	**Ca** (mg/l)	**Na** (mg/l)	**Mg** (mg/l)	**Cu** (mg/l)	**Fe** (mg/l)	**Cl** (mg/l)	**H_2T** (g/l)	**pH**	**TA** (g/l)	**VA** (g/l)
Cation exchange Resins	**	*	ns	**	*	**	ns	**	ns	ns	ns	ns	ns	ns	ns	ns
R1-H	7.0b	0.109b	98.0a	-0.64a	6.46b	406a	55a	16a	57a	0.14a	1.1a	33a	3.5a	2.80a	6.6a	0.29a
R2-H	6.7a	0.107a	98.1a	-0.53	6.28a	416b	56a	18b	56a	0.13a	1.1a	32a	3.5a	2.82a	6.6a	0.30a
Proportion of treated wine (%)	**	**	ns	**	**	**	**	**	**	**	**	ns	**	**	**	**
0	7.3d	0.105a	98.1a	-0.66c	6.64c	559f	76e	25d	76e	0.18b	1.4d	31a	3.6b	3.08e	6.3a	0.37d
5	7.2d	0.105a	98.0a	-0.68c	6.56bc	534e	75e	23d	71d	0.17b	1.4d	32a	3.6b	3.03de	6.4b	0.35d
10	7.2d	0.109ab	98.0a	-0.59b	6.58bc	497d	68d	21c	66c	0.15b	1.3d	31a	3.6b	2.99d	6.5c	0.34cd
15	7.1c	0.110ab	98.0a	-0.59b	6.46bc	466c	61c	19c	66c	0.15b	1.2c	32a	3.6b	2.94c	6.5d	0.32c
25	6.9b	0.113b	98.0a	-0.56b	6.36bc	410b	52b	15b	60b	0.13b	1.0b	31a	3.5b	2.86b	6.6e	0.29b
100	5.9a	0.106a	98.1a	-0.46a	5.60a	0a	0a	0a	1a	0.04a	0.2a	31a	3.2a	1.96a	7.4f	0.10a
Interaction	ns	**	**	**	*	**	ns	ns	**	**	ns	ns	**	**	**	*

Treatment means were separated by Scheffée test at the 5% significance level. Different letters in the same column indicate statistically significant differences: * ($p \leq 0.05$), ** ($p \leq 0.01$), ns-not significant

R1 and R2 - cation exchange resins in hydrogen form; resin volume = 100 mL; flow = 6 $ml.min^{-1}$

Ipt - Total phenols index; A_{420} - Absorbance at 420 nm; L*, a* and b* - CIELAB cordinates; H_2T - Tartaric Acid; TA - Titrable Acidity; VA - Volatile Acidity

J. Int. Sci. Vigne Vin, 2006, **40**, n°4, 223-246

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table VII - Main effects of ion-exchange resins and different proportions of treated and untreated white wine B by cation and anion exchange on some wine characteristics

Influence du double exchange cationique-anionique et des proportions croissantes de vin traité sur les caractéristiques du vin B

20)	L*	a*	b*	K (mg/l)	Ca (mg/l)	Na (mg/l)	Mg (mg/l)	Cu (mg/l)	Fe (mg/l)	Cl (mg/l)	pH	TA (g/l)	VA (g/l)	H_2T (g/l)	Mal. Ac. (g/l)	Shik Ac. (g/l)	Lact. Ac. (g/l)	Citric Ac. (g/l)
	ns	ns	ns	*	ns	**	ns	ns	ns	ns	*	ns	**	ns	ns	ns	ns	ns
1a	98.3a	-0.48a	5.69a	410a	54a	16a	60a	0.15a	1.1a	33a	2.93a	6.1a	0.38b	3.0a	2.0a	37a	1.1a	894a
8a	98.3a	-0.39a	5.47a	416b	56a	18b	59a	0.14a	1.0a	34a	2.96b	6.1a	0.35a	2.9a	2.0a	36a	1.1a	895a
	**	*	**	**	**	**	**	**	**	ns	**	**	**	**	*	ns	**	**
8b	98.0a	-0.59b	6.60c	550f	76d	24e	74d	0.18b	1.3d	31a	3.10c	6.3c	0.40c	3.4d	2.1b	37a	1.4b	1001b
1b	97.9a	-0.47b	6.54c	532e	72cd	22d	73d	0.17b	1.3d	31a	3.09c	6.3c	0.40c	3.2cd	2.0a	36a	1.2b	979b
7b	98.0a	-0.44b	6.36bc	501d	68cd	20cd	71cd	0.16b	1.2cd	32a	3.06bc	6.2bc	0.39bc	3.2cd	2.1b	37a	1.2b	975b
4b	98.0a	-0.41b	6.17b	471c	61bc	19bc	66bc	0.16b	1.1bc	33a	3.04bc	6.2bc	0.35bc	3.1bc	2.0a	36a	1.2b	960b
6b	98.3a	-0.40b	5.66b	417b	52b	17b	61b	0.14b	1.1b	35a	3.00b	6.1b	0.36b	2.9b	1.9ab	36a	1.1b	885b
0a	99.5b	-0.30a	2.13a	7a	2a	0a	11a	0.06a	0.2a	42a	2.40a	5.4a	0.29a	1.8a	1.8a	35a	0.5a	578a
	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	*	ns	ns	ns	ns	ns

Treatment means were separated by Scheffée test at the 5% significance level. Different letters in the same column indicate statistically significant differences: * ($p \leq 0.05$), ** ($p \leq 0.01$), ns-not significant

R1, R2 - cation exchange resins in H+ form; R3 - anion exchange resin in OH- form¸ resin volume = 100 mL; flow = 6 $ml.min^{-1}$

Ipt - Total phenols index; A_{420} - Absorbance at 420 nm; L*, a* and b* - CIELAB cordinates; TA - Titrable Acidity; VA - Volatile Acidity, H_2T - Tartaric Acid; Mal. Ac- * Malic acid; Lact. Ac. - Lactic acid.

In order to examine the effect of the ion exchange treatments in the tartrate stability, phenolic, mineral and organic acid composition, the eluted wines were partially blended with untreated wine, to produce lots with different proportions of treated wine. We have studied if the different lots were stable, without significant modifications in the sensory attributes and also it they satisfied the requirements of the OIV (1995).

1) White wines

The results using R1 resin in magnesium or sodium form, comparatively to R2 resin (in H^+ form) are reported in table V (wine A). According to the results obtained in the first year of assays, we have used in the 2nd year R1 and R2 resins only in H^+ form. The characterizations of wines resulting from the mixture of treated wine with R1 or R2 resins are presented in table VI (wine B). The results obtained by double ion-exchange resins are reported in table VII.

a) Effects in the phenolic content and wine chromatic characteristics

The comparison of the R1 resin in magnesium and sodium form and R2 resin (table V) indicated that the wine resulting from the mixture of the control wine with the treated wine with R1-Mg resin was higher in total phenolic content as well as the absorbance at 420 nm than lots resultant of the mixtures of treated wine with others resins. Concerning the wine B (table VI), the R2 resin showed higher adsorption of the phenolic compounds than R1. About the wine chromatic characteristics we have obtained no differences in the lightness, but significant variations in A_{420} as well as a* and b* coordinates.

As it can be observed, when the percentage of treated wine in the mixture increased, the phenolic compounds decreased significantly, as compared to control wine. The absorbance at 420 nm slightly decreased in wine A and slightly increased in wine B; probably these variations are related to the adsorption of wine compounds in the resins matrix and also with the pH wine variation. In both wines (A and B), the a* coordinate increased along with the percentage of treated wine and the b* decreased. The results showed that the treated wines were significantly different than the control wine; however, wines with different proportions of treated wine presented intermediate characteristics between the control wine and 100 % of treated wine. These results are consistent with those obtained by MOURGUES (1993), WEINDARD and DEDARDEL (1994) and BENITEZ *et al.* (2002a, b).

The two groups of resins (R1+R3) and (R2+R3) showed similar behaviour relatively to phenolic constituents and wine chromatic characteristics. As the percentage of treated wine in the mixtures increased, the concentration in total phenols decreased; however this decrease was higher in the double ion exchange than in the cation exchange. The results revealed a slight increase in the lightness, and decrease in the a* and b* coordinates, possibly due to some retention of the wine constituents in the resin matrix (table VII).

b) Effect in the mineral composition

Confirming the previous assays, R1-Na and R2-H resins have shown more ability than R1-Mg in removing the potassium.

As expected, the wine treated with R1-Na resin showed higher sodium content, as already shown. The concentration of sodium in the 25 % of treated wine was 204 mg/l, while for 100 % was 480 mg/l confirming the large release of this cation to the wine, although the treated wine with R1-Mg presented high magnesium content.

When both resins were in the H^+ form (table VI), the resins revealed good affinity to potassium and calcium and some to iron, when the percentage of treated wine in the lots increased, the cation contents decreased, and the wine pH lowered. For the 100 % treated wine, the sum of cations was < 2 mg/l and the pH < 2.0. As suggested by PALACIOS *et al.* (2001b) and BENITEZ *et al.* (2002a) the reduction in phenolic compounds content and the partial elimination of metal cations in the wines, as iron and copper, are interesting to increase the oxidative stability, which is especially important mainly in white wines.

As expected, there weren't any significant differences in the chloride anion content in the wines treated with cation resins.

The results obtained for double exchange, with the two groups of resins, confirm those presented with the cation exchange. As the percentage of treated wine in the mixtures increased, the concentration in cations decreased; nevertheless, the variation in chlorides content was not significant.

c) Effect in pH, titratable and volatile acidity

The lots with wines treated with resins in Mg^{2+} or Na^+ forms showed no significant variations in pH values. The wines treated with resins in acid cycle presented a significant decrease in pH to values low 2.0, although the mixtures with a certain percentage of treated wine revealed some decrease in pH, but never more than 0.3 pH units, as established by OIV (1995, 1998). The wines showed a slight increase in total acidity due to the increase in concentration of the H^+. This is an important aspect to wines produced in countries with hot climate, which is the case of Portugal, as suggested by MIRANDA PATO

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table VIII - Tartrate stability evaluation of the mixtures in different proportions of treated and untreated white wine by cation exchange resins, by cation and anion exchange resins and cold treatment (temperature of saturation and mini-contact test)

Évaluation de la stabilité tartrique des vins avec proportions croissantes de vin traité par résines cationiques et du vin stabilisé par le froid (méthode de la température de saturation ou test de mini-contact)

	White Wine A			White Wine B							
	R1-Mg	R1-Na	R2-H	R1-H		R2-H		R1+R3		R2+R3	
Proportion of treated wine (%)	Tsat test	Tsat test	Tsat test	Mini contact test	Tsat test	Mini contact test	Tsat test	Mini contact test	Tsat test	Mini contact test	Tsat test
0	Instable (18.8 °C)	Instable (18.8 °C)	Instable (18.8 °C)	Instable (11.6 %)	Instable (19.3 °C)	Instable (11.6 %)	Instable (19.3 °C)	Instable (10.2 %)	Instable (17.4 °C)	Instable (10.2 %)	Instable (17.4 °C)
5	Instable (18.8 °C)	Instable (19.0 °C)	Instable (18.6 °C)	Stable (3.3 %)	Instable (15.0 °C)	Instable (5.6 %)	Instable (17.3 °C)	Stable (4.7 %)	Instable (13.1 °C)	Instable (5.7 %)	Instable (15.7 °C)
10	Instable (18.0 °C)	Instable (17.5 °C)	Instable (17.2 °C)	Stable (4.9 %)	Stable (11.0 °C)	Stable (3.9 %)	Instable (17.1 °C)	Stable (4.1 %)	Stable (12.2 °C)	Stable (3.2 %)	Instable (15.3 °C)
15	Instable (15.8 °C)	Instable (17.7 °C)	Instable (17.0 °C)	Stable (3.8 %)	Stable (11.0 °C)	Stable (3.4 %)	Instable (17.1 °C)	Stable (3.4 %)	Stable (11.6 °C)	Stable (4.9 %)	Instable (15.8 °C)
25	Instable (15.7 °C)	Instable (15.4 °C)	Stable (12.5 °C)	Stable (2.1 %)	Stable (8.0 °C)	Stable (2.2 %)	Stable (12.4 °C)	Stable (1.6 %)	Stable (8.4 °C)	Stable (3.3 %)	Stable (8.7 °C)
Standard Cold Treatment (4 weeks at 0°C)	Instable (13.1 °C)			Instable (11.8 %)				Tsat = 20.3 °C (instable)			

R1-Na cation exchange resin in sodium form; R1-Mg cation exchange resin in magnesium form; R2 - cation exchange resin in hydrogen form

©Vigne et Vin Publications Internationales (Bordeaux, France)

(1961) and MOURGUES (1993). In addition, we have verified a slight decrease in volatile acidity.

For double cation-anion exchange, the wine pH suffered a slight reduction with increment in the percentage of treated wine. However, the pH did not decrease more than 0.3 pH units in the studied percentages, what is in accordance with the imposed restrictions from OIV (1995). As the percentage of treated wine in the mixtures increased, the titrable and volatile acidity decreased comparatively to the control wine.

d) Effect in the organic acid composition

No important differences in organic acid concentration were observed for both resins in different forms and any percentages of treated wine (data no shown).

It can be observed that the two groups of resins had a similar behaviour in what concerns to the organic acid composition (table VII). The results showed that, except to shikimic acid, as the percentage of treated wine in the mixtures increased, the organic acids content decreased.

e) Wine tartrate stability evaluation

The results of wine tartrate stabilization are presented in table VIII; we can see the values of the temperatures of saturation for the different wines (A and B wines) as well as the results of the Boulton test for wine B. As it can be observed to wine A, no percentage of treated wine with R1-Mg and R1-Na has revealed stable. Only the 25 % wine treated with R2 resin was stable. For wine B, the tartrate stability was evaluated by two methods, nevertheless different results were obtained. The results of mini-contact method revealed that the totality of the wine lots which were treated with R1 resin were stable, while for mixtures with wine treated with R2 resin, only the mixtures with more than 5 % of treated wine showed stability. Concerning the results to the temperature of saturation showed that the mixtures were stable with 10 % treated wine with R1-H but required 25 % of treated wine with R2 resin. This is in accordance with our previous works, where the highest affinities to potassium and calcium with R1 resin was evidenced. The cold treatment (one month at 0 ºC) was not enough to stabilize the wine, which can be explained by the fact that a treatment at 0 ºC have not been sufficient to induce the tartrate salts precipitation or probably this was also due to an abnormal content of protector colloids in the wine.

The results for the double cation-anion revealed for mini-contact method, the treated wines with (R1+R3) resins were stable for all proportions, while using (R2+R3) resins only the wines with more than 5 % treated wine showed stables. However, according to the results of saturation temperature, the wines with mixture of treated wine using (R1+R3) resins were stable for proportions higher than 5 %, while for wine treated with (R2+R3) resins only the wine with 25 % of treated wine was stable. This is in accordance with our previous work with cation exchanger resins; therefore the double cation-anion exchange did not present better results than the cation exchange.

f) Sensory evaluation

In table IX, we present the average of the scores of treated wines with different cationic resins, and also the average of the different percentages of treated wine. No significant differences in sensory attributes of the mixtures were observed.

2) Red wines

The results using R1 resin in magnesium form comparatively to R2 resin (in H^+ form) are reported in table X (wine A), and the results using both resins in H^+ form are presented in table XI (wine B).

a) Effects in the phenolic composition and wine chromatics characteristics

The ion exchange influences to certain extent, the phenolic compounds and chromatic characteristics. The slight decrease in the phenol compounds, verified with the increase of the percentage of treated wine in lots, was evidenced by the diminution in total phenol concentration, anthocyanins content and by the decrease in pigment colour, probably due to some pigments retention in the resins' surface, which is in conformity with the results obtained by other authors (WALKER *et al.*, 2002, BENITEZ *et al*., 2002a). In addition, we observed an increase in polymerized pigments, possibly explained by the retention of small pigments, like the monomeric anthocyanins in the resins. In order to examine the effect of ion exchange treatments in the anthocyanins composition, an HPLC analysis was carried out for wine B. The results are reported in table XII. We can observe that the wines treated with R1 resin showed higher reduction in anthocyanins contents than the wines treated with R2, confirming the results obtained for total anthocyanins. Generally, the content of theses all compounds decreased along with the increase in treated wine, and the eluted wine (100 %) presented significantly lower contents of these compounds. The group of the 3-monoglucosides has presented the highest reduction, probably due to the highest concentration in wine.

On the other hand, the verified diminution in the wine pH is able to influence the chromatic characteristics; what this is consistent with the work of HERNÁNDEZ and MÍNGUEZ (1997). The ion exchange increased the colour intensity and decreased the tonality, what was also observed by WALKER *et al.* (2002).

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table IX - Sensory analysis results of the wine stabilized by cation exchange resins. Values of the scores from 1 (minimum) to 5 (maximum) for each attribute, except global appreciation that is from 1 to 20

Résultats de l'analyse sensorielle des vins stabilisés par résines échangeuses de cations. Classification de 1 (minimum) à 5 (maximum) pour chaque attribut, excepté appréciation globale (de 1 à 20)

	Proportion of treated wine (%)	Visual			Nose			Taste			Global appreciation		
		R1-Na	R1-Mg	R2-H	R1-Na	R1-Mg	R2-H	R1-Na	R1-Mg	R2-H	R1-Na	R1-Mg	R2-H
White Wine (A)	0	3.8	3.7	3.6	3.1	2.9	3.0	3.0	3.0	3.0	13.0	13.1	12.9
	5	3.6	3.6	3.6	3.0	2.9	2.6	2.8	2.8	2.8	12.6	12.9	12.6
	10	3.9	3.6	3.7	2.8	2.8	2.9	3.0	2.4	2.8	13.0	11.8	12.1
	15	3.9	3.6	3.7	3.0	2.6	3.0	2.9	2.8	3.0	12.9	12.8	12.9
	25	3.8	3.8	3.7	2.8	2.8	2.9	3.0	3.0	3.0	13.0	13.2	12.8
Red Wine (A)	0	a	3.8	3.8	a	3.1	3.1	a	2.9	2.9	a	12.9	12.9
	5	a	3.9	3.9	a	3.0	3.0	a	2.7	2.9	a	12.8	13.1
	10	a	3.8	3.8	a	2.9	3.2	a	2.8	2.9	a	13.0	13.2
	15	a	3.7	3.9	a	2.4	3.2	a	2.7	2.9	a	11.8	13.4
	25	a	3.8	3.9	a	3.2	3.2	a	2.9	3.0	a	13.0	12.9

R1-Na cation exchange resin in sodium form; R1-Mg cation exchange resin in magnesium form; R2 - cation exchange resin in hydrogen form; a - not evaluated.

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table X - Main effects of cation-exchange resins and proportions of treated wine on some red wine A characteristics

Influence des résines échangeuses de cations et des proportions croissantes de vin traité sur les caractéristiques du vin A

Treatment	Ipt	Int. (ua)	Ton. (ua)	L*	a*	b*	ANT (mg/L Mv-3-Glc.)	PGT (ua)	IPP (%)	K (mg/l)	Ca (mg/l)	Na (mg/l)	Mg (mg/l)	Cu (mg/l)	Fe (mg/l)	Cl (mg/l)	pH	TA (g/l)	VA (g/l)	H_2T (g/l)
Resins	ns	**	**	ns	**	**	ns	**	**	**	**	**	**	ns	**	ns	**	**	ns	ns
R1-Mg	59.5a	10.50a	0.663b	66.9a	36.39a	1.68b	231.3a	21.78b	61b	1024b	59b	11b	92b	0.05a	3.8b	35a	3.42b	6.3a	0.54a	2.3a
R2-H	58.5a	11.17b	0.616a	66.4a	39.30b	1.35a	239.6a	18.87a	57a	822a	55a	8a	49a	0.05a	3.6a	35a	3.34a	6.5b	0.53a	2.3a
Proportion of treated wine (%)	**	**	**	ns	**	**	**	*	**	**	**	**	**	ns	**	ns	**	**	**	ns
0	59.5b	10.46a	0.671e	66.2a	37.23ab	1.15a	268.6c	22.23b	57a	1137c	87c	14d	65a	0.05a	4.7e	35a	3.41b	6.3a	0.57b	2.3a
5	59.6b	10.45a	0.665de	67.4a	36.13a	1.43ab	246.9bc	20.79b	57a	1133c	71b	12cd	66a	0.05a	4.5de	35a	3.40b	6.3a	0.53a	2.3a
10	59.6b	10.51ab	0.658d	66.8a	37.14ab	1.48b	251.7bc	19.37b	58a	1018bc	65b	10bcd	66a	0.04a	4.3d	35a	3.40b	6.4b	0.53a	2.3a
15	59.4b	10.63b	0.650c	66.7a	37.32ab	1.54bc	235.8b	21.25b	59a	1016bc	63ab	7ab	66a	0.05a	4.1c	34a	3.36ab	6.4bc	0.53a	2.3a
25	59.3b	10.79c	0.636b	66.4a	38.19b	1.67bc	229.3b	20.64b	59a	904b	54a	9bc	69a	0.04a	3.7b	35a	3.31a	6.5c	0.52a	2.3a
100	56.5a	12.17d	0.557a	66.6a	41.05c	1.81c	180.3a	17.67a	64b	329a	nd	3.5a	92b	0.05a	0.8a	35a	na	na	na	na
Interaction	ns	**	**	ns	**	**	**	ns	**	**	*	ns	**	ns	*	ns	**	**	**	ns

Treatment means were separated by Scheffée test at the 5% significance level. Different letters in the same column indicate statistically significant differences: * ($p \leq 0.05$), ** ($p \leq 0.01$), ns-not significant, nd-not detected; na- not analysed

R1-Mg: cation exchange resin in Mg^{2+} form; R2 - cation exchange resin in H^+ form; resin volume = 50 mL; flow = 2.7 $ml.min^{-1}$

Ipt- total phenols index; Int - colour intensity; Ton - Tonality; L*;a*, b* - CIELAB coordinates; Ant - Total Anthocyanins (express mg/L Malvidin-3-glucoside); PGT - Total pigments colour; IPP - Polymerized Pigments Index; K - potassium; Ca - Calcium; Na - Sodium; Mg - Magnesium; Cu - Copper; Fe - Iron; Cl - Chloride; H2T - Tartaric Acid; TA - Titrable Acidity (g/L tartrate acid); VA - Volatile Acidity (g/L acetic acid).

J. Int. Sci. Vigne Vin, 2006, **40**, n°4, 223-246

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table XI - Main effects of cation-exchange resins and proportions of treated wine on some red wine B characteristics

Influence des résines échangeuses de cations et des proportions croissantes de vin traité sur les caractéristiques du vin B

Treatment	Ipt	Int. (ua)	Ton. (ua)	L*	a*	b*	ANT (mg/L Mv-3-Glc.)	PGT (ua)	IPP (%)	K (mg/l)	Ca (mg/l)	Na (mg/l)	Mg (mg/l)	Cu (mg/l)	Fe (mg/l)	Cl (mg/l)	pH	TA (g/l)	VA (g/l)	H_2T (g/l)
Resins	ns	**	**	**	**	**	**	**	**	ns	**	ns	**	ns	**	ns	**	ns	ns	ns
R1-H	48.1a	11.19b	0.579b	66.3a	41.03b	-1.19a	337.6a	26.24a	48b	636a	39a	13a	74b	0.03a	2.9b	35a	3.01b	5.6a	0.66a	2.6a
R2-H	48.5a	11.61a	0.569a	67.5b	40.06a	-0.95b	361.8b	29.15b	45a	640a	44b	12a	72a	0.03a	2.5a	35a	2.93a	5.7a	0.65a	2.6a
Proportion of treated wine (%)	**	**	**	**	**	ns	**	**	**	**	**	**	**	ns	**	ns	**	**	**	ns
0	51.4d	10.35a	0.628f	68.5c	36.13a	-0.98a	379.6d	28.88c	46a	870e	61f	19f	97e	0.03a	3.6e	35a	3.32f	5.3a	0.72e	2.6a
5	50.1c	10.55ab	0.618e	68.4c	36.08ab	-0.90a	376.3d	28.40c	46a	833d	55e	17e	92d	0.03a	3.4de	35a	3.27e	5.4b	0.70d	2.6a
10	49.6c	10.61ab	0.605d	68.1c	37.66bc	-1.04a	367.4c	27.69b	46a	764c	51d	15d	89c	0.03a	3.2cd	35a	3.21d	5.4b	0.69cd	2.6a
15	49.67c	10.82bc	0.592c	67.6bc	38.74c	-1.20a	366.2c	27.29b	46a	722b	44c	13c	85b	0.03a	3.1c	35a	3.16c	5.5c	0.68c	2.6a
25	47.9b	11.06c	0.569b	66.9b	40.66d	-1.32a	355.6b	27.77b	46a	640a	38b	11b	74a	0.03a	2.7b	35a	3.04b	5.7d	0.64b	2.6a
100	42.2a	15.01d	0.430a	61.9a	53.28e	-0.96a	252.9a	24.16a	51b	nd	2a	2a	nd	0.02a	0.4a	34a	1.83a	6.7e	0.39a	2.5a
Interaction	**	**	**	**	**	**	**	**	**	ns	ns	**	**	ns	ns	ns	*	**	ns	ns

Treatment means were separated by Scheffée test at the 5% significance level. Different letters in the same column indicate statistically significant differences: * ($p \leq 0.05$), ** ($p \leq 0.01$), ns-not significant, nd-not detected

R1-H: cation exchange resin in H^+ form; R2 - cation exchange resin in H^+ form; resin volume = 100 mL; flow = 6 $ml.min^{-1}$

Ipt- total phenols index; Int - colour intensity; Ton - Tonality; L*, a*, b* - CIELAB coordinates; Ant - Total Anthocyanins (express mg/L Malvidin-3-glucoside); PGT - Total pigments colour; IPP - Polymerized Pigments Index; K - potassium; Ca - Calcium; Na - Sodium; Mg - Magnesium; Cu - Copper; Fe - Iron; Cl - Chloride; H2T - Tartaric Acid; TA - Titrable Acidity (g/L tartrate acid); VA - Volatile Acidity (g/L acetic acid).

Table XII - Main effects of ion-exchange resins and proportions of treated wine on monomeric anthocyanins (mg/L) of red wine B

Influence des résines échangeuses d'ions et des proportions croissantes de vin traité sur les anthocyanines monomériques (mg/L) du vin B

Treatment	Df3 glc	Cy3 glc	Pt3 gclc	Pn3 glc	Mv3 glc	∑ *Monoglucosides*	Df3acg lc	Pt3acg lc	Pn3ac glc	Mv3ac glc	∑ *Acetic acid esters*	Df3cm glc	Pt3 cm glc	Pn3 cmglc	Mv3 cmglc	∑ *Coumaric acid esters*	Mv3gl cpy
Resins	**	**	**	**	**	**	*	ns	ns	ns	ns	**	ns	*	**	**	**
R1-H	15.9a	3.7a	17.4a	20.2a	97.2a	154.1a	1.4a	1.9a	1.9a	4.0a	9.3a	2.2a	2.7a	3.9a	12.0a	20.8a	3.4a
R2-H	17.1b	3.9b	18.9b	22.0b	106.3b	168.2b	1.5b	1.9a	1.9a	4.1a	10.0a	2.4b	2.8a	4.2b	12.9b	22.2b	3.6b
Proportion of treated wine (%)	**	**	**	**	**	**	**	ns	**	**	**	**	**	**	**	**	**
0	19.4d	4.3d	21.5d	25.4e	121.8d	192.4c	1.8b	1.9a	2.2c	4.8d	10.8a	2.5c	2.8b	4.5c	14.0b	23.8b	3.6b
5	18.6c	4.2cd	20.5c	23.8d	113.9c	181.0bc	1.7a	1.9a	1.9b	4.5c	10.6b	2.4b	2.9b	4.3bc	13.4b	22.9b	3.6b
10	18.0c	4.1c	19.8c	22.9bc	109.9bc	175.7bc	1.7a	1.9a	1.9b	4.4bc	10.0b	2.4b	2.8b	4.2bc	13.1b	22.5b	3.6b
15	18.0c	4.1c	20.1c	23.5d	113.5c	179.2bc	1.7a	1.9a	1.9b	4.6cd	10.0b	2.4b	2.9b	4.4bc	13.8b	23.5b	3.5b
25	16.7b	3.9b	18.6b	21.5b	104.4b	165.1b	1.7a	1.9a	1.9b	4.2b	9.8b	2.4b	2.8b	4.2b	13.0b	22.3b	3.5b
100	7.1a	2.4a	8.3a	9.4a	47.2a	74.4a	nd	1.9a	1.8a	1.9a	5.7a	1.9a	2.1a	2.6a	7.4a	13.9a	3.2a
Resins	*	ns	*	ns	*	*	*	ns	ns	ns	ns	**	ns	ns	ns	ns	**
R1+R3	14.9a	3.6a	16.3a	18.8a	89.4a	142.9a	1.4a	1.91a	1.9a	3.9a	9.1a	2.2a	2.6a	3.7 a	10.8a	19.3a	3.4a
R2+R3	15.3b	3.7a	16.8b	19.4a	92.9b	148.1b	1.5b	1.91a	1.9a	3.9a	9.2a	2.2b	2.6a	3.7a	11.1a	19.7a	3.5b
Proportion of treated wine (%)	**	**	**	**	**	**	**	**	**	**	**	**	**	**	**	**	**
0	19.0e	4.2e	20.6e	24.0e	113.8e	181.6d	1.8b	1.9b	2.0b	4.5e	10.2e	2.4c	2.9d	4.3d	13.1d	22.6d	3.6d
5	18.2d	4.1de	19.8d	22.9de	109.0de	174.1d	1.7a	1.9b	1.9b	4.4de	10.0d	2.3c	2.8cd	4.2d	12.8d	22.1cd	3.6d
10	17.7d	4.0d	19.4d	22.4d	107.1d	170.6cd	1.7a	1.9b	1.9b	4.3cd	9.9cd	2.3c	2.8cd	4.1cd	12.6cd	21.8cd	3.6cd
15	16.7c	3.9c	18.4c	21.1c	101.6c	161.7c	1.7a	1.9b	1.9b	4.2c	9.7c	2.3b	2.8c	3.9bc	12.0c	21.0bc	3.5c
25	15.4b	3.7b	16.9b	19.2b	92.6b	147.6b	1.7a	1.9b	1.9b	3.9b	9.5b	2.2b	2.6b	3.7b	11.2b	19.8b	3.5b
100	3.5a	1.9a	4.1a	5.1a	22.9a	37.4a	nd	1.8a	1.7a	1.9a	5.4a	1.6a	1.7a	2.1a	4.1a	9.5a	2.8a

Treatment means were separated by Scheffée test at the 5 % significance level. Different letters in the same column indicate statistically significant differences: * ($p \leq 0.05$), ** ($p \leq 0.01$), ns-not significant, nd - not detected. R1 and R2 - cation exchange resins in H^+ form; R3 - anion exchange resin in OH^- form

Df3glc: Delphinidin-3-monoglucoside; Cy3glc: Cyanidin-3-monoglucoside; Pt3gclc: Petunidin-3-monoglucoside; Pn3glc: Peonidin-3-monoglucoside; Mv3glc: Malvidin-3-monoglucoside; sum of the 3-monoglucosides of the Df, Cy, Pt, Pn, Mv; Df3acglc: Delphinidin-3-monoglucoside-acetate; Pt3acglc: Petunidin-3-monoglucoside-acetate; Pn3acglc: Peonidin-3-monoglucoside-acetate; Mv3acglc: Malvidin-3-monoglucoside-acetate; ∑ Acetic acid esters - Sum of the acetic acid esters; Df3cmglc: Delphinidin-3-monoglucoside-p-coumarate; Pt3cmglc: Petunidin-3-monoglucoside-p-coumarate; Pn3cmglc: Peonidin-3-monoglucoside-p-coumarate; Mv3cmglc: Malvidin-3-monoglucoside-coumarate; ∑ Coumaric acid esters - sum of the Coumaric acid esters; Mv3glcpy: Malvidin-3-monoglucoside-piruvate (Vitisin A).

J. Int. Sci. Vigne Vin, 2006, **40**, n°4, 223-246

©Vigne et Vin Publications Internationales (Bordeaux, France)

Table XIII - Main Effects of Double cation-anion exchange resins and proportions of treated wine on red wine B characteristics

Influence du double échange cationique-anionique et des proportions croissantes de vin traité sur la composition du vin B

Treatment	Ipt	Int. (ua)	Ton. (ua)	L*	a*	b*	ANT	PGT (ua)	IPP (%)	K (mg/l)	Ca (mg/l)	Na (mg/l)	Mg (mg/l)	Cu (mg/l)	Fe (mg/l)	Cl (mg/l)	pH	TA (g/l)	VA (g/l)	H_2T (g/l)	Lact Ac. (g/l)	Citr Ac. (g/l)
Resins	**	**	ns	ns	ns	*	ns	*	**	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	ns	ns
R1+R3	49.5b	10.07a	0.543a	67.5a	38.74a	-0.59a	334.6a	25.25a	45a	636a	38a	14a	77b	0.02a	2.9a	32b	3.17a	5.3a	0.69a	2.2a	3.0a	916a
R2+R3	46.5a	11.78b	0.563a	67.9a	38.63a	-0.93b	337.6a	27.84b	48b	647a	41a	13a	74a	0.03a	2.9a	30a	3.17a	5.3a	0.69a	2.3a	3.1a	943a
Proportion of treated wine (%)	**	ns	*	ns	**	**	**	**	**	**	**	**	**	**	**	*	**	ns	**	**	ns	**
0	52.5c	10.58a	0.585b	68.3a	36.23a	-0.98a	383.5d	28.88b	45a	871f	55b	20c	100f	0.04b	3.7e	36c	3.39f	5.3a	0.73c	2.5b	3.2a	999b
5	52.1c	11.26a	0.569b	67.4a	37.76a	-0.12a	374.2cd	28.28b	45a	827e	52b	18c	97e	0.04b	3.6d	36c	3.37e	5.3a	0.71bc	2.5b	3.2a	954b
10	51.3c	10.82a	0.560ab	67.3a	37.85a	-0.93b	366.7bcd	28.93b	47ab	778d	48ab	16b	91d	0.04b	3.4d	35c	3.34d	5.3a	0.71bc	2.5b	3.3a	933ab
15	50.1bc	10.67a	0.547ab	67.8a	37.49a	-1.00b	352.1bc	28.24b	46a	733c	43ab	15b	85c	0.03ab	3.3c	34c	3.31c	5.3a	0.70bc	2.5b	3.1a	927ab
25	48.4b	10.70a	0.563ab	67.9a	38.23a	-0.83a	341.3b	25.27b	46a	639b	38a	13a	78b	0.01a	2.9b	31b	3.25b	5.3a	0.68b	2.3b	3.2a	911ab
100	33.6a	11.55a	0.494a	67.6a	44.56b	0.36b	198.6a	17.57a	49b	1a	nd	nd	2a	0.01a	0.3a	16a	2.37a	5.3a	0.62a	1.1a	2.8a	855a
Interaction	ns	*	**	ns	ns	ns	ns	ns	**	**	ns	**	**	*	ns	ns	ns	ns	ns	ns	ns	ns

Treatment means were separated by Scheffée test at the 5 % significance level. Different letters in the same column indicate statistically significant differences: * ($p \leq 0.05$), ** ($p \leq 0.01$), ns-not significant, nd-not detected.

R1, R2 - cation exchange resins in H+ form; R3 - anion exchange resin in OH^- form. Resin volume = 100 mL; flow = 6 $ml.min^{-1}$.

Ipt- total phenols index; Int - colour intensity; Ton - Tonality; L*, a*, b* - CIELAB coordinates; Ant - Total Anthocyanins (express mg/L Malvidin-3-glucoside); PGT - Total pigments colour; IPP - Polymerized Pigments Index; K - potassium; Ca - Calcium; Na - Sodium; Mg - Magnesium; Cu - Copper; Fe - Iron; Cl - Chloride; H2T - Tartaric Acid; TA - Titrable Acidity (g/L tartrate acid), VA - Volatile Acidity (g/L acetic acid).

Table XIV - Tartrate stability results of red wine treated with cation exchanger's resins, cation and anion exchange resins and cold treatment (mini-contact and temperature of saturation)

Évaluation de la stabilité tartrique des vins avec proportions croissantes de vin traité par résines cationiques et du vin stabilisé par le froid (méthode de la température de saturation et du test de mini-contact)

	Red Wine A				Red Wine B							
	R1-Mg		R2-H		R1-H		R2-H		R1+R3		R2+R3	
Proportion of treated wine (%)	**Mini contact test**	**Tsat test**	**Mini contact test**	**Tsat test**	**Mini contact test**	**Tsat test**	**Mini contact test**	**Tsat test**	**Mini contact test**	**Tsat test**	**Mini contact test**	**Tsat test**
0	Instable (10.2 %)	Instable (25.2°C)	Instable (10.2%)	Instable (25.2°C)	Instable (5.6 %)	Instable (23.3°C)	Instable (5.6 %)	Instable (23.3°C)	Instable (5.6 %)	Instable (23.0°C)	Instable (5.6 %)	Instable (23.0°C)
5	Instable (8.3 %)	Instable (25.0°C)	Stable (2.2 %)	Instable (24.4°C)	Stable (3.1 %)	Stable (18.8°C)	Stable (4.8 %)	Stable (21.5°C)	Stable (3.2 %)	Stable (17.8°C)	Stable (3.2 %)	Stable (19.0°C)
10	Stable (3.3 %	Instable (24.7°C)	Stable (4.5 %)	Instable (23.3°C)	Stable (2.9 %)	Stable (18.6°C)	Stable (3.2 %)	Stable (20.8°C)	Stable (2.5 %)	Stable (17.0°C)	Stable (4.4 %)	Stable (18.7°C)
15	Stable (2.5 %)	Instable (25.1°C)	Stable (3.8 %)	Instable (23.0°C)	Stable (2.1 %)	Stable (14.6°C)	Stable (2.7 %)	Stable (18.0°C)	Stable (2.1 %)	Stable (13.8°C)	Stable (4.4 %)	Stable (18.4°C)
25	Stable (1.3 %)	Instable (24.9°C)	Stable (3.4 %)	Stable (21.1°C)	Stable (1.9 %)	Stable (13.5°C)	Stable (2.1 %)	Stable (16.8°C)	Stable (2.0 %)	Stable (12.8°C)	Stable (3.9 %)	Stable (12.5°C)
Standard cold treatment	Instable (> 5%)… Tsat = 23.1 °C (Instable)				Stable (2.5 %)				Tsat = 20.2 °C (Stable)			

R1-Mg cation exchange resin in magnesium form; R1 and R2 - cation exchange resins in H^+ form; R3 - anion exchange resin in OH^- form
R1 and R2 - cation exchange resins in H+ form.

J. Int. Sci. Vigne Vin, 2006, **40**, n°4, 223-246

©Vigne et Vin Publications Internationales (Bordeaux, France)

To double cation-anionic exchange (table XIII), the two groups of resins (R1+R3) and (R2+R3) had quite similar behaviour. Comparatively to a cation exchange, the double exchange showed higher pigments adsorption, presumably because the exposed surface is higher. The decrease in total phenol content, total anthocyanins concentration and total pigments increased with the percentage of treated wine. In what respects the individual anthocyanins (table XII), the two groups of resins have a similar behaviour for several anthocyanins confirming the result obtained to the total anthocyanins concentration. However, as was verified above, the individual anthocyanins concentration decreased along with an increase in percentage of treated wine, indicating the retention of these compounds in the resins matrix. The results of anthocyanins families showed that the double cation-anion exchange removed more anthocyanins than the cation exchange, except for esters with acetic acid.

b) Effect in the mineral composition

The R1 resin in Mg^{2+} form showed to be less efficient than in H^+ form or R2-H resin to potassium removal, once the affinity to resin increases with the cation valence (WEINAND and DEDARDEL, 1994); this may have implications in the tartrate stabilization.

When the two resins were used in H^+ form (table XI), the resins presented similar behaviour concerning the potassium cation, nevertheless the R1 resin removed more calcium than R2, and the R2 resin showed to remove more magnesium and iron than R1. The resins didn't show any affinity to copper. As the percentage of treated wine in the lots increased, the cation contents decreased significantly. As expected, there weren't significant differences in the concentration of chloride anion of the wines treated with cationic resins, as already observed in white wines.

The double exchange (table XIII) showed results similar to be obtained in experiments with cationic resins. It was verified that R3 removed a certain quantity of chloride anion, so the treated wine presented less quantity of this anion comparatively to the control wine.

c) Effect in the organic acid composition

As expected, the cation resins did not influence the organic acids content (data not shown). In double exchange (table XIII), only tartaric and citric acids were removed with anion resin, as it was also observed for the white wine.

d) Effect in pH, titrable and volatile acidity

According to the previous observations, the wine pH decreased with an increase of the percentage of treated wine; however we have verified that the pH didn't decrease to values below 3.0 and didn't decreased to more than 0.3 pH units in any of the studied proportions, according to the imposed limitations of the OIV (1995). The titrable acidity increased along with the increase H^+ content in wine submitted to cation exchange. This can be a positive aspect to wines produced in countries with hot climate, as suggested by MIRANDA PATO (1961) and MOURGUES (1993). As observed to white wines, we have verified some decrease in the volatile acidity, which is difficult to explain using the cation exchange.

The effect of the double ionic exchange in pH, titrable and volatile acidity is reported in table XIII. As in cation exchange, the wine pH decreased with a proportion of treated wine, but more slowly, although never decreased to values less than 2.37. However, the titrable acidity presented no significant differences as observed in white wines. The volatile acidity of the wines decreased slightly with a proportion of treated wine, and the eluted wine presented significant differences comparatively to the control wine as was verified with the white wine and cation exchange.

e) Sensory evaluation

Only the wine A was submitted to sensory evaluation by panel taste. The average of the scores, of the attributes of the wines with different percentages of treated wine with R1-Mg and R2-H resins, are presented in table IX. The data indicated there were no significant differences between treated wines and control wine. The panel taste indicated that the wines with highest proportion in treated wine (25 %) are not significantly different from the control wine. However, further research is needed to investigate if and why the ion exchange affects the sensory attributes of the wine, particularly the double cation-anion exchange.

f) Wine tartrate stability evaluation

The results of tartrate wine stabilization are presented in table XIV. For wine A, the two used methods for evaluation of the tartrate stability gave different results. Through the mini-contact test, only the wines with more than 5 % of treated wine with R1 resin presented stable, while for treated wine with R2, the 5 % was enough to stabilize the wine. However, according to the saturation temperature method, the wines with mixture of treated wine with R1 resin were not stable, whereas only the wine with 25 % of treated wine with R2 resin was stable.

The wine B became stable for all proportions and for the two resins, as well as by cold stabilization.

Using double cation-anion exchange, the wine became stable for all the proportions and for the two groups of

©Vigne et Vin Publications Internationales (Bordeaux, France)

resins, as well as when using the classic process, in accordance with the observed with the cation exchange resins.

CONCLUSION

The R2 resin showed to be more efficient to enhance the tartrate stabilization than R1 in Mg^{2+} form; however in H^+ form, the behaviour of both resins was similar. Both resins presented a good retention for K^+ and for Ca^{2+}, the main cations implicated in wine tartrate instability. In respect of the double cation-anion exchange, the results about tartrate stabilization were similar to those obtained with only cation exchange resins.

The assembled wines presented a slight decrease in the concentration of total phenols, higher in double exchange, due to the retention of some phenol compounds in the resin surface. Some differences were also observed in chromatic characteristics, which can be due to the variation in pH and to the retention of some wine constituents. A trained panel has not found differences between treated and untreated wines. In fact, the cation exchange did not affect negatively the wine quality attributes, which is an interesting result on a practical point of view.

The technology of cation exchange resins in H^+ form is an effective procedure for tartrate stabilization of wines, respecting the limitations imposed by OIV. In addition, the wines were stabilized concerning tartrate precipitations, using cation exchange resins in H^+ form, without previous cold treatment, which could be really an alternative oenological practice, especially when considering also economical and energy aspects.

Acknowledgements : The authors thank to the AGRO Program (project nº23, measure 8.1 of the Ministry of the Agriculture of Portugal) for the financial support of this work; to PRODEP - Action 5.3 - Advanced training of university teachers (Ministry of Education of Portugal); to Comissão Vitivinícola Regional do Ribatejo (CVRR) for providing the wines, to CVRR panel tasters and to Multifiltra (Lisboa, Portugal) for giving us the resins. Special thanks to Mr. Inácio Dias (Ecohídrica, Lisboa, Portugal) for the collaboration to this study.

REFERENCES

AUSTERWEIL G.V., 1953. Quelques méthodes d'application des échangeurs d'ions en œnologie. *Ind. Alim. Agric.*, 197-207.

AUSTERWEIL G.V., 1955. Applications des échangeurs aux boissons alimentaires. *In : L'échange d'ions et les échangeurs*, ed. Gauthier-Villars (Paris) pp. 214-235.

BENITEZ J.G., PALACIOS MACIAS V.M., PAZO J.A. and RODRÍGUEZ J.A.S., 2002a. Industrial development of proton exchange for tartrate stabilization of sherry wines. *Eur Food Res Technol*., **214**, 418-422.

BENITEZ P., CASTRO R. and BARROSO C.G., 2002b. Removal of iron, copper and manganese from white wines through ion exchange techniques: effects on their organoleptic characteristics and susceptibility to browning. *Anal. Chim. Acta*, **458**, 197-202.

BLOUIN J., GUIMBERTEAU G. and AUDOUIT P., 1979. Prévention des précipitations tartriques dans les vins par le procédé par contact. *Connaissance Vigne Vin*, **13**, 149-169.

BONORDEN W. R., NAGEL, C. W. and POWERS, J. R., 1986. The adjustment of high pH/high titrable acidity wines by ion exchange. *Am. J. Enol. Vitic*., **37**, 143-149.

BOULTON R., 1982. La cinétique de la précipitation du bitartrate de potassium des vins. *Rev Fr Œnol.*, **87**, 97-100.

BURNETT J., 1982. 20 ans d'évolution des techniques de stabilisation au froid. *Rev. fr. Œnol*, **87**, 103-104.

CAMEIRA DOS SANTOS P., MENDES PEREIRA O., GONÇALVES F., TOMÁS SIMÕES J. and DE PINHO M.N., 2000. Ensaios de estabilização tartárica em vinhos portugueses: estudo comparativo da electrodiálise e de um método tradicional. *Ciência Tec. Vitiv.*, **15**, 95-108.

CAPUTI, M.A., 1994. Résines échangeuses d'ions cations. Feuillet vert 980. OIV, Paris.

COLAGRANDE O., 2002. Stabilità chimico-fisica dei vini. *Industrie delle Bevande*, **XXXI**, 238-250.

DAL CIN G., 1984. La pratica dello scambio ionico nel tratamento dei vini destinati alla aromatizzazione. *R. Vitic. Enol*., **3**, 115-133.

ESCUDIER J. L., MOUTOUNET M., BARILLERE J.M., BENARD P., COTTEREAU P., AUDINOS R., *et al*., 1985. L'électrodialyse : déminéralisation et désacidification des moûts de raisin, fabrication de moûts concentrés rectifiés. *Rev. fr. Œnol*., (cahier scientifique), **106**, 39-44.

FEUILLAT M. and CHARPENTIER C., 1998. Les mannoprotéines de levures : un adjuvant œnologique possible. *Bull. OIV*, **813-814**, 945-951.

GLORIES Y., 1978. Recherches sur la matière colorante des vins rouges. *Thèse de doctorat* de l'Université de Bordeaux II, Bordeaux.

HERNÁNDEZ P. and MÍNGUEZ S., 1997. Uso de resinas de intercambio iónico en enologia. Estabilización tartárica. *Rev. Fr. Œnol.*, **162**, 32-35.

IONESCU, T. D., 1969. Échangeurs d'ions en œnologie. *Bull. OIV*, 465, 1180-1196.

LEE T.H., 1991. L'utilisation de l'échange d'ions dans l'industrie du vin australien. *Communication presented at the Wine Technology Expert Group of OIV*.

LUBBERS S., LÉGER A., CHARPENTIER C. and FEUILLAT M., 1993a. Effet colloïde-protecteur d'extraits de parois de levures sur la stabilité tartrique d'une solution hydro-alcoolique modèle. *J. Int. Sci. Vigne Vin*, **27**, 13-22.

MAUJEAN A., SAUSY L. and VALLÉE D., 1985. Détermination de la sursaturation en bitartrate de potassium d'un vin. Quantification des effets colloïdes-protecteurs. *Rev. Fr. Œnol.*, **100** (4), 39-50.

MAUJEAN A., 1994. Traitement par le froid artificiel des vins en relation avec leur stabilisation vis-à-vis des troubles cristallins tartriques. *In: Les acquisitions récentes dans les traitements physiques du vin. Incidences sur la composition*

 ©Vigne et Vin Publications Internationales (Bordeaux, France)

chimique et les caractères organoleptiques des vins. Ed. B. Donèche, Tec & Doc, (Lavoisier, Paris) pp. 81-102.

McLAREN K., 1980. Food Colourimetry. *In: Developments in Food Colours*. J. Walford Ed.; Applied Science Publisher: London, U.K., vol. 1, p.27-45.

MÍNGUEZ S. and HERNÁNDEZ, P., 1998. Tartaric stabilization of red, rosé, white wines with $L^{(+)}$- Calcium tartrate crystal seeding. *Am. J. Enol. Vitic*., **49** (2), 177-182.

MOINE-LEDOUX V., PERRIN A., PALADIN, I. and DUBOURDIEU D., 1997. First result of tartaric stabilization by adding mannoproteins (Mannostab™). *J. Int. Sci. Vigne Vin*, **31**, 23-31.

MOINE-LEDOUX V. and DUBOURDIEU D., 2002a. Rôle des mannoprotéines de levures vis-à-vis de la stabilisation tartrique des vins. *Bull OIV*, **857-858**, 471-482.

MOINE-LEDOUX V. and DUBOURDIEU D., 2002b. Une mannoprotéine à ancre GPI responsable de la stabilisation tartrique des vins. Derniers développements industriels. *Rev. Fr. Œnol.*, **193**, 32-35.

MOREIRA J.L., MARCOS A.M. and BARROS P., 2002a. Analysis of Portuguese wines by Fourier Transform Infrared Spectrometry (FTIR). *Ciência Tec. Vitiv.*, **17** (1), 27-33.

MOREIRA J.L., MARCOS A.M. and BARROS P., 2002b. Proficiency test on FTIR wine analysis. *Ciência Tec. Vitiv*., **17** (2), 41-51.

MOURGUES J., 1993. Utilisation des résines échangeuses d'ions. *Rev Œnol*., **69**, 51-54.

MOUTOUNET M., SAINT-PIERRE B., BATLLE J. L. and ESCUDIER J. L., 1997. Le stabilisateur tartrique : principe et description du procédé. *Rev. fr. Œnol*., **162**, 15-17.

PALACIOS V.M., CARO I. and PÉREZ L., 2001a. Application of ion exchange techniques to industrial process of metal ions removal from wine. *Adsorption*, **7**, 131-138.

PALACIOS V.M., CARO I. and PÉREZ L., 2001b. Application of ion exchange techniques to industrial process of must acidification. *Sep Purif Méthodes*, **30**, 143-156.

OIV, 1990. Recueil des méthodes internationales d'analyse des vins et des moûts. *Office International de la Vigne et du Vin* (Paris): 368 p.

OIV, 1995. *Résolution OENO 4/95: Résines échangeuses de cations*.

OIV, 1998. International Code of oenological practices. Office International de la Vigne et du Vin, Paris.

RANKINE, B. C., 1985. Using ion exchange for prevention of tartrate precipitation in wine. *Aust. Grapegrower Winemaker*, **263**, 18-21.

RIBÉREAU-GAYON P. and STONESTREET E., 1965. Les dosages des anthocyanes dans le vin rouge. *Bull. Société Chimie*, **9**, 2649-2652.

RIBÉREAU-GAYON J. and PEYNAUD E., 1966. *Traité d'œnologie*, II. Ed. Libr. Polytechnique CH. Beranger.

RIBÉREAU-GAYON P., 1970. Le dosage des composés phénoliques totaux dans les vins rouges. *Chimie Analytique*, **52**, 627-631.

RIBÉREAU-GAYON J., PEYNAUD E., RIBÉREAU-GAYON P. and SUDRAUD P., 1977. Stabilisation des vins vis-à-vis des précipitations tartriques. *In : Traité d'Oenologie, Sciences et techniques du vin* - tome 4, éd. Dunod (Paris) pp. 347-374.

RIBÉREAU-GAYON P., GLORIES Y., MAUJEAN A. and DUBOURDIEU, D. (1998). *In : Traité d'Œnologie. 2- Chimie du vin*, éd. Dunod (Paris), pp.438-445

SERRANO M., SUDRAUD P. and RIBÉREAU-GAYON P., 1983. Prévention des précipitations tartriques dans les vins au moyen du traitement en continu par le froid. *Connaissance Vigne Vin*, **17**, 121-136.

SOMERS T.C. and EVANS M.E., 1977. Spectral evaluation of young red wines: anthocyanin equilibria, total phenolics, free and molecular SO_2, « Chemical age ». *J. Sci. Food Agric*, **28**, 279-287.

TAMBORINI A. and MAGRO A., 1970. Il trattamento dei vini con resine scambiatrici e il rapporto potassio: sodio. *Rivista di Viticiltura e di Enologia*, 89-94.

TUSSEAU D. and BENOIT C., 1986a. Analyse collaborative des acides organiques des moûts et des vins par HPLC. *Feuillet Vert 800. OIV*, Paris.

TUSSEAU, D. and BENOIT C., 1986b. Analyse collaborative des acides organiques des moûts et des vins par HPLC. *Feuillet Vert 813. OIV*, Paris.

VIALATTE C., 1984. Bitartrate de potassium. Test de Boulton. *Rev Fr Œnol*., 34, 20.

WALKER T., MORRIS J., THRELFALL R. and MAIN G., 2002. pH Modification of Cynthiana wine using cationic exchange. *J. Agric. Food Chem*., **50**, 6346-5352.

WEINAND R. and DEDARDEL F., 1994. Ion exchange resins and polymeric adsorbents in the beverage industry. *In : Les acquisitions récentes dans les traitements physiques du vin. Incidences sur la composition chimique et les caractères organoleptiques des vins*. Ed. B. Donèche, Tec & Doc (Lavoisier, Paris), pp 23-41.

WUCHERPFENNING K., 1973. Emploi de l'acide métatartrique pour la stabilisation du vin. *Bull. OIV*, **506**, 330-339.

WURDIG G., MULLER T. and FRIEDRICH G., 1982. Méthode pour caractériser la stabilité du vin vis-à-vis du tartre par détermination de la température de saturation. *Bulletin de l'OIV*, **613**, 220-229.

Manuscrit reçu le 16 octobre 2006 ; accepté pour publication, après modifications le 27 novembre 2006

©Vigne et Vin Publications Internationales (Bordeaux, France)