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RESEARCH PAPER

The use of cation exchange resins in wines: Effects on pH, tartrate stability, and metal content

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Abstract

F. Ponce, Y. Mirabal-Gallardo, A. Versari, and V.F. Laurie. 2018. The use of cation exchange resins in wines: Effects on pH, tartrate stability, and metal content. Cien. Inv. Agr. 45(1): 82-92. Treating wines with cation exchange resins allows the reduction of pH and contributes to limiting the formation of tartrate salts by exchanging cations such as potassium with hydrogen ions. This manuscript summarizes the results of a series of laboratory and winery-scale trials performed with the aim of evaluating the ion exchange process and its effects on the chemical composition of the treated samples. The laboratory-scale results showed that both the procedure employed for the activation of resins and the chemical composition of the wines affected the extent of the chemical changes occurring during the treatment. As such, the winery-scale trials showed that the resin-treated wines have significantly lower pH, higher total acidity, less tartrate formation (measured by weight), and a reduced amount of most metals analyzed. Wine samples blended with approximately 20% of cation exchange-treated samples (by volume) showed no signs of tartrate instability when assessed by a quick qualitative cold test.

Keywords: Ion exchange resins, metals, pH, tartrate stability, wine.

Introduction

Wine pH has a remarkable effect on the quality of the final product, influencing its chemical, microbial and sensorial stability. High pH wines are less tolerant to microbial spoilage, in need of higher amounts of sulfites, less stable aromatically, and have a diminished potential shelf life (Bartowsky, 2009; Boulton *et al.,* 1996; de Orduña, 2010). Nevertheless, high pH wines are not uncommon, as some producers prefer to work with ripened fruit as a way to avoid certain vegetal nuances and the characteristic astringency of less mature grapes (Bindon *et al.,* 2013; Romero *et al.,* 2006). Likewise, the establishment of short-cycle grape varieties in warm areas and the rising temperatures of some viticultural regions could be exacerbating the occurrence of high pH wines (de Orduña *et al.,* 2010; Hannah *et al.,* 2013; Webb *et al.,* 2012).

Another winemaking issue that is closely linked with the acidity of wines is the development of

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insoluble salts, resulting from the reaction of anionic tartrates and cations such as potassium or calcium (i.e., potassium bitartrate, KHT, or calcium tartrate, CaT) (Boulton *et al*., 2006; Ibeas *et al*., 2015). The concentration of these cations in wines may be as variable as 125–2040 mg L^{-1} for K^{+}, and 50–300 mg L^{-1} for Ca^{2+} (Ough *et al*., 1982; Pohl, 2007; Laurie *et al*., 2010), and their upper concentration range represents a higher risk of tartrate salts formation. If this phenomenon is not addressed during winemaking, these crystals may appear as deposits at the bottom of the bottles, thus possibly causing consumer rejection (Boulton *et al.,* 2006).

In regard to solving these issues, the lowering of wine pH is most typically performed by the addition of tartaric acid, unless titratable acidity is high. Instead, preventative solutions to avoid tartrate precipitation in commercial wines range from the use of chemicals to physical means such as cold stabilization (Boulton *et al.,* 2006; Mira *et al.,* 2006). One of the alternatives available to simultaneously lower the pH, reduce the concentration of cations, and limit the formation of tartrate salts is the use of cation exchange resins (Bordeu and Cristi, 2001; Benitez *et al.,* 2002; Mira *et al.,* 2006; Lasanta *et al.,* 2013; Ibeas *et al.,* 2015). These substances are comprised of a polymeric matrix onto which different ionized functional groups could be attached, depending on the type of exchange required (i.e., carboxylic acid or sulfonic acid for acidic resins and various types of amino groups for basic exchangers) (Esau and Amerine, 1966; Mira *et al.,* 2006). These charged functional groups are neutralized by ions of the opposite sign that can be exchanged for ions of equivalent charge present in the treated samples (Esau and Amerine, 1966; Mira *et al.,* 2006; Boulton *et al.,* 2006). In conventional wine treatment, the resin beads are activated with a strong acid solution such as sulfuric or hydrochloric acid, rinsed with soft water, and loaded with the sample to be treated. As the wine is passed through the column, the hydrogen ions (H^{+}) loaded onto the resins are exchanged by wine cations, such as potassium or calcium (K^{+}, Ca^{2+}), thus causing a reduction of wine pH, cation concentration, and a reduced likelihood of the formation of tartrate salts (Palacios *et al.,* 2001; Walker *et al.,* 2002; Benitez *et al.,* 2002; Mira *et al.,* 2006; Lasanta *et al.,* 2013; Ibeas *et al.,* 2015).

According to the regulations of the International Organization of Vine and Wine, OIV, cation exchange treatments must not alter the nature of the wine and should avoid significant reductions in color intensity, metallic content (>300 mg L^{-1}), and pH (should remain above 3.0 and its total decrease should not exceed 0.3 units). The treatment must not leave foreign substances in the wine or impart characteristics that are unusual; and when used for acidification, this should not increase more than 54 meq L^{-1} (OIV, 2016 a-c).

Given that the chemical composition of the wine samples and the operating conditions of the equipment may vary widely, we developed a series of laboratory and commercial-scale trials with the aims of testing the ion exchange process and evaluating its effects on the pH, metal content, and formation of tartrate salts on the resulting wines.

Materials and methods

Reagents and materials

Laboratory-scale treatments were done using the "ion exchanger I" (Reag. pH Eur., Merck, Darmstadt, Germany), three fritted columns (length: 24 cm; diameter: 4 cm; frit pore size: 40–100 µm; stopcock bore size: 4 mm; stopcock plug size: 15.2/30 mm), sulfuric acid (95–97% p.a., Emsure®, Merck), and ultra-pure water (Millipore, Darmstadt, Germany). Additionally, commercial-scale trials were conducted in a Juclas-Vason MMPH2013 system (Verona, Italy) equipped with a proprietary defined cationic resin, using 50% sulfuric acid (Proquiel,

Santiago, Chile), and softened water produced on site (<45 ppm $CaCO_3$).

The analyses of metals required the use of nitric acid (HNO_3 65%, Sigma-Aldrich, Darmstadt, Germany), hydrogen peroxide (H_2O_2 30%, Sigma-Aldrich), lanthanum oxide (La_2O_3, Merck), certified solutions of metals (i.e., K, Na, Mg, Ca, Fe, Zn, Cu and Mn; 1000 mg L^{-1}; Spex Industries Inc., Edison, Metuchen, New Jersey, USA), HNO_3 (Merck), and various types of glassware. Other analyses required the use of plastic cuvettes UV 230–900 nm (Sigma-Aldrich), PVDF syringe filters (13 mm; 0,45 µm; Merck), iodine 1N Titripu® (Merck), potassium L-tartrate monobasic (99%; Aldrich), sodium disulfate p.a. ACS reagent (98–100.5%; Merck), a UV-Vis spectrophotometer Pharo 300 Spectroquant®, pH and conductivity meters (HI 2002 y 2003, Hanna, Woonsocket, Rhode Island, USA), and various types of glassware.

Laboratory-scale trials

Evaluation of the resin activation protocol

The following trials were performed to evaluate the effects of using different volumes and concentrations of sulfuric acid during the activation of resins: three fritted columns, representing three replications, were loaded with 10.7 ± 0.37 g of hydrated resins corresponding to approximately 10 mL of the resin base volume, which were activated with 1.25, 2.5, or 5 mL of H_2SO_4 for each mL of the resin base, either at 20 or 50% v/v concentration. Once the resins were activated and rinsed with 10 mL of distilled water, the columns were loaded with 150 mL of Sauvignon Blanc or Petit Verdot wine samples (Table 1). To avoid sample contamination with sulfuric acid, the first 30 mL of treated wine was discarded. Finally, the flow of wine passing through the resin was regulated to approximately 40.1 ± 0.76 mL min^{-1}. The pH of the different wine fractions was measured every 10 mL until 100 mL of treated wine was collected.

Table 1. Wine samples used for the laboratory and industrial-scale trials

Wine samples	Vintage	Ethanol	pH	Total acidity	Volatile acidity	Free SO_2	Total SO_2	Reducing sugars
		% V/V		g/L H_2SO_4	g/L CH_3COOH	mg/L	mg/L	g/L
Laboratory-scale trials								
Evalution of the resin activation protocol								
Sauvignon blanc	2017	12,8	3,3	3,6	0,32	34	155	1,3
Petit verdot	2017	13,6	3,9	2,7	0,49	30	49	2,7
Effects of the resins on the chemical composition of the treated wines								
Chardonnay	2016	13,5	3,4	3,1	0,37	33	134	2,1
Sauvignon blanc	2016	12,9	3,4	3,3	0,30	34	128	1,8
Merlot	2016	12,8	3,7	3,1	0,51	30	64	2,1
Cabernet Sauvignon	2016	12,8	3,8	2,9	0,53	28	58	2,6
Industrial-scale trial								
Effects of the resins on the chemical composition of the treated wines								
Chardonnay	2016	13,7	3,7	3,0	0,38	19	41	2,1
Sauvignon blanc	2016	12,9	3,3	3,4	0,31	12	125	2,0
Merlot	2016	12,8	3,7	3,3	0,49	12	35	1,4
Cabernet Sauvignon	2016	14,1	3,7	3,2	0,48	12	35	2,1
Effects of the resins on wine pH and conductivity								
Chardonnay	2017	13,3	3,3	3,5	0,37	35	154	2,3

Effects of the resins on the chemical composition of the treated wines

Wine samples of the varieties Sauvignon Blanc, Chardonnay, Merlot, and Cabernet Sauvignon (Table 1) were subjected to a laboratory-scale resin treatment as explained before (resin activation protocol). The treated samples were blended with untreated leftovers to complete three bottles of 700 mL wine per treatment and variety, as follows: T0: 100% untreated wine; T1: 5% resin treated wine blended with 95% untreated wine; T2: 10% resin treated wine blended with 90% untreated wine; T3: 20% resin treated wine blended with 80% untreated wine; and T4: 100% resin treated wine. As indicated before, all treatments were replicated three times, and the wines were analyzed for pH, total acidity, and metal content, as detailed below.

Industrial-scale trials

Effects of the resins on the chemical composition of the treated wines

Similarly to the experiment outlined in the previous section, four different wines of the varieties Sauvignon Blanc, Chardonnay, Merlot, and Cabernet Sauvignon (Table 1) were used to test an industrial cation exchange resin equipment as follows: 1000 liters of resins were hydrated for 12 h with softened water, followed by activation with 250 L of 50% sulfuric acid, which allowed the treatment of approximately 10,000 L of wine. The acidic solution was maintained in contact with the resins for 10 min to charge them with hydrogen ions, after which an automatic acid sweep was carried out with compressed air, a rinse with 1,000 L of soft water produced in-house (<45 ppm $CaCO_3$), and a new sweep with air to eliminate the sulfuric acid and water residues generated during this process. As an extra precautionary measure, the first 225 L of each wine batch were discarded to ensure the elimination of water and acid present from the previous steps. As indicated before, 10,000 L of wine was treated per exchange cycle, initiating with the white varieties and making sure that the resins were cleaned and regenerated before a new batch of wine was treated.

At the end of the process, the treated wines were mixed with the untreated wine remnants as follows: T0: 100% untreated wine; T1: 5% resin treated wine blended with 95% untreated wine; T2: 10% resin treated wine blended with 90% untreated wine; T3: 20% resin treated wine blended with 80% untreated wine; and T4: 100% resin treated wine. In this case, in addition to the analyses of pH, total acidity, and metal content, the number of samples available allowed us to evaluate the formation of tartrates in the treated wines. As before, all the treatments were replicated three times.

Evaluations and analyses

General wine analyses: Alcohol concentration, pH, titratable acidity, volatile acidity, reducing sugars, free and total SO_2, and electrical conductivity were done following the official protocols described elsewhere (OIV, 2009).

Analyses of wine metals: The analyses of Ca, K, Na, Mg, Cu, Mn, Fe and Zn were performed with an AAS (280 FAAS, Agilent Technologies) under the following operating conditions: Air and acetylene flow, 13.50/2.00 L min^{-1}; burner height and still width, 13.5 and 0.2–1.0 mm; lamp current, 4–10 mA; and wavelengths for metals determination (nm), K: 766.5, Na: 589.0, Ca: 422.7, Cu: 324.8, Mg: 285.2, Mn: 270.5, Fe: 248.3, Zn: 213.9. Moreover, calibration curves were prepared from standard solutions of each metal resulting in coefficients of determinations above 0.997 (i.e., Ca, 1–25 mg L^{-1}; Mg, 0.25–5 mg L^{-1}; K, 2–20 mg L^{-1}; Na, 1–10 mg L^{-1}, Mn, 1–6 mg L^{-1}, Cu, 0.5–5 mg L^{-1}, Fe, 1–10 mg L^{-1}, Zn, 0.5–3 mg L^{-1}). The measurements of Ca, Mg, K and Na required a 1:10 dilution of the samples with the La_2O_3 (1.1 g L^{-1} solution), while all other metals were measured with no dilution. Before the analyses, the samples were digested in a microwave oven (CEM Mars Xpress) to eliminate organic interferences as follows: 5 mL of wine, 3 mL of 65% HNO_3 and 1.5 mL of H_2O_2 30% were

placed in 55 mL Teflon® tubes with agitation. The heating program of the microwave oven consisted of a first ramp time of 5 min going from 20 to 175 °C with a 3 min hold time, followed by a 5 min ramp from 175 to 30 °C with a hold time of 3 min (this cycle was repeated twice at 800 W of applied power). Once digested, the samples were diluted to 50 mL with ultra-pure water and each wine sample was analyzed three times.

Tartrate salts formation

One hundred mL samples were placed in 200 mL beakers, to which 0.4 g of potassium bitartrate were added (99.5–100.5%, Sigma-Aldrich). The samples were stirred by means of an agitator (Stirrer HI190M, Hanna) for 30 min at -4 °C in a cooling jacketed beaker (RW05525G, Arquimed). Subsequently, they were maintained for 48 h at -4 °C in a refrigerated incubator (Scientific precision 815, Cambridge Scientific). To quantify the mass of the tartrate crystals formed, the wine was filtered using nitrocellulose membrane discs (0.45 µm, 47 mm; Merck), which were dried inside glass Petri dishes (80 mm × 15 mm; Brand) by direct heat for five min at 45 °C. The mass of the tartrates formed was obtained by the difference between the final weight minus the mass of the membrane discs and the 0.4 g of potassium bitartrate used to facilitate the nucleation of the crystals.

The qualitative stability of the tested wines was also checked by holding the samples for three days at -4 °C in a conventional freezer (OIV, 2009). The samples that showed the formation of crystalline deposits that did not re-dissolve once the temperature of the wine warmed up to room temperature were considered unstable. This qualitative test was chosen as a quick way to estimate tartrate stability and supplement the results of tartrate formation measured by weight.

Data analyses

The results obtained were statistically compared using one-way analysis of variance (ANOVA, followed by Tukey test). The statistical analyses were performed using the free software R, version 3.3.3 (The R foundation).

Results and discussion

Laboratory-scale trials

Evaluation of the resin activation protocol

As indicated before, the volume of the resin base was fixed to 10 mL to allow the treatment of at least 100 mL of wine. To avoid contamination of the sample with sulfuric acid, the first 30 mL of treated wine (i.e., equivalent to 3 volumes of resin) was eliminated, as the pH of these fractions was significantly lower than the rest of the wine.

The results of these trials showed that the magnitude and duration of the cation exchange effect, as measured by the variation in the samples' pH, were larger than the volume (i.e., 1.25, 2.5, and 5 mL of H_2SO_4 per mL of resins) and concentration of sulfuric acid solution (i.e., 50 instead of 20%) increased (Figure 1). The results obtained for both wine varieties were consistent, showing that higher volumes or concentrations of sulfuric acid resulted in wines with lower pH. Moreover, in most cases, the initial pH of the treated wines remained stable for at least 5 volumes of treated wine (i.e., 50 mL of wine), after which larger deviations were observed for the treatments in which smaller volumes or concentrations of sulfuric acid were used for the resin activation (Figure 1). Regardless, the pH of the treated wines remained well below that of the untreated samples. The former is an indication that the exchange capacity of the resins should be periodically checked to avoid significant efficiency losses by, for example, continuous monitoring of the pH of the wine being treated.

During these trials, we also evaluated whether a varying flow of wine through the column influences the results, but no differences were found among wine flows between 23.0 ± 1.77 and 40.1 ± 0.76 mL min^{-1} (results not shown).

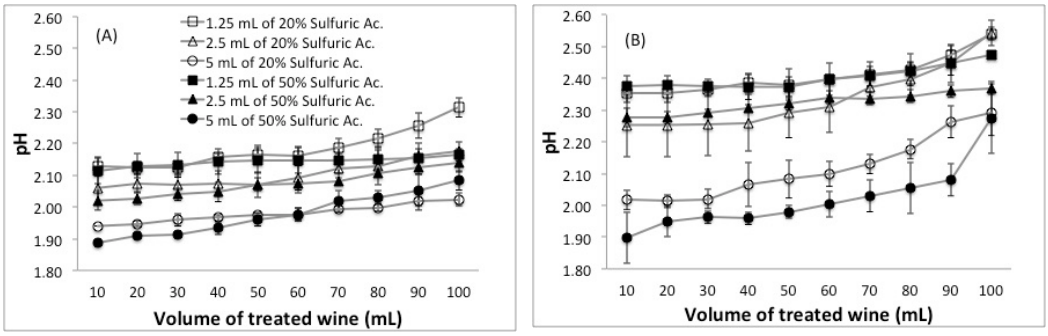

Figure 1. Variation in wine pH during the treatment of (A) Sauvignon blanc and (B) Petit verdot wine with cation exchange resins activated with different volumes (i.e., 1.25, 2.5, or 5 mL) and concentrations of sulfuric acid solution (i.e., 20 or 50%).

Effects of the resins on the chemical composition of the treated wines

The cation exchange treatments significantly reduced the pH, increased the acidity, and lowered the content of most metals analyzed (Table 2). For instance, treatment T3 (20% of resin-treated wine) showed pH reductions between 5 and 7%, and total acidity increased between 10 and 17%. Thus, depending on the metal analyzed, the 20% resin-treated wine showed concentration reductions varying from 14 to almost 75% (i.e., K and Cu content respectively, in Chardonnay wine). These results are in agreement with those obtained at a winery-scale (Table 3), as detailed and discussed in the following section.

Industrial-scale trials

Effects of the resins on the chemical composition of the treated wines

In agreement with previous reports (Mira *et al.,* 2006, Lasanta *et al.,* 2013, Ibeas *et al.,* 2015), Table 3 shows a decrease in pH with a concomitant increase in total acidity as the proportion of cation exchange-treated wine increased from T0 to T4. For instance, treatment T3 (i.e., 20% of resin-treated wine) showed reductions of pH between 6 and 7%, and increases in total acidity between 9 and 16%, depending on the samples tested. Correspondingly, a decrease in electrical conductivity was seen as the proportion of resin treated wine increased up to 20% (T3). Instead, treatment T4 showed conductivity values even higher than the untreated samples, even though they contained significantly less cations (Table 3).

This result prompted us to conduct another experiment to check the variation in pH and electrical conductivity of wines blended at 10% increments with wines treated with cation exchange (Figure 2). This experiment was performed at a laboratory-scale with a Chardonnay wine (Table 1), showing a continuous trend of pH decrease and a breakpoint in the reduction of conductivity of approximately 50%, after which the conductivity started to rise (Figure 2). The initial decrease in conductivity is consistent with a lower number of cations conducting electricity, as the proportion of resin-treated wine increases. The later rise in electrical conductivity is explained by the higher mobility of the hydrogen ions (H^+) compared to other cations (Lee and Rasaiah, 2011). At low pH, the H^+ are significantly more abundant, and given their higher mobility, they can quickly reach the electrodes of the probe, producing a conductivity rise.

Given that the measurements of electrical conductivity were proven unsatisfactory as a way to estimate tartrate stability, the formation of tartrates was evaluated by weight. In this case, it can be seen that as the proportion of resin-treated wine increased from 0 to 100% (T0 to T4), the amount of tartrates formed was significantly reduced, reaching values close to zero for treatment 4

Table 2. Chemical and mineral composition of white and red wines treated with cation exchange resins at a laboratory-scale setting.

Wine type & composition	Percentage of wine treated with cation exchange resins as part of a blend with untreated wine (%)										
	0 (T0)		5 (T1)		10 (T2)		20 (T3)		100 (T4)		*p* value
(A) Sauvignon blanc											
pH	3.40±0.01	e	3.36±0.01	d	3.32±0.00	c	3.23±0.14	b	1.99±0.01	a	<0.001
TA (g/L H2SO4)	3.29±0.05	a	3.37±0.01	b	3.49±0.01	c	3.77±0.03	d	4.55±0.03	e	<0.001
K (mg/L)	684.10±7.02	d	635±9.2	c	616.33±28.05	c	548±17.14	b	40.57±19.4	a	<0.001
Ca (mg/L)	72.13±5.83	c	63.6±1.74	bc	61.83±1.66	b	54±2.44	b	12±4.28	a	<0.001
Fe (mg/L)	1.39±0.24	c	1.10±0.09	bc	0.98±0.18	bc	0.68±0.30	ab	0.16±0.08	a	<0.001
Cu (mg/L)	0.32±0.07	b	0.22±0.10	ab	0.14±0.02	a	0.13±0.04	ab	0.09±0.07	a	0.018
Na (mg/L)	8.13±0.70	c	7.53±1.8	bc	6.87±1.39	bc	5.07±0.64	b	0.8±0.2	a	<0.001
Mg (mg/L)	75.67±0.25	d	72.43±1	cd	70.07±0.68	c	62.57±1.4	b	8.67±3.11	a	<0.001
Mn (mg/L)	1.02±0.12	c	0.80±0.28	bc	0.57±0.04	ac	0.52±0.18	ab	0.22±0.19	a	0.001
Zn (mg/L)	0.77±0.02	d	0.73±0.02	cd	0.67±0.05	c	0.57±0.04	b	0.12±0.02	a	<0.001
(B) Chardonnay											
pH	3.38±0.00	e	3.35±0.01	d	3.31±0.01	c	3.23±0.00	b	2.11±0.02	a	<0.001
TA (g/L H2SO4)	3.09±0.00	a	3.13±0.00	b	3.26±0.00	c	3.41±0.00	d	4.50±0.01	e	<0.001
K (mg/L)	994.73±41.21	c	991.8±11.96	c	965.6±24.56	c	853.27±10.42	b	33.4±27.09	a	<0.001
Ca (mg/L)	46.05±0.87	b	43.15±0.98	b	39.98±4.67	b	37.85±5.01	b	11.08±1.81	a	<0.001
Fe (mg/L)	0.48±0.18	a	0.32±0.18	a	0.25±0.02	a	0.22±0.11	a	0.15±0.04	a	0.06
Cu (mg/L)	0.4±0.23	a	0.17±0.15	a	0.1±0.09	a	0.06±0.05	a	0.05±0.03	a	0.04
Na (mg/L)	18.41±1.73	c	17.99±0.59	c	17.31±0.86	bc	14.98±0.67	b	3.54±0.40	a	<0.001
Mg (mg/L)	85.87±4.65	c	81.23±1.89	c	79.83±2.39	c	70.37±1.33	b	6.93±4.37	a	<0.001
Mn (mg/L)	1.1±0.24	b	1.02±0.06	b	0.92±0.24	b	0.88±0.11	b	0.03±0.03	a	<0.001
Zn (mg/L)	1±0.02	c	0.93±0.01	c	0.92±0.04	c	0.81±0.03	b	0.12±0.05	a	<0.001
(C) Merlot											
pH	3.72±0.00	d	3.65±0.03	cd	3.59±0.01	c	3.44±0.01	b	2.13±0.09	a	<0.001
TA (g/L H2SO4)	3.07±0.10	a	3.09±0.03	b	3.22±0.05	c	3.40±0.07	d	5.17±0.10	e	<0.001
K (mg/L)	1175.43±12.62	d	1117.17±23.07	cd	990.33±121.83	bc	948.90±16.01	b	34.17±19.73	a	<0.001
Ca (mg/L)	49.05±3.8	c	43.18±5.03	bc	38.11±0.93	b	33.64±0.88	b	8.72±6.01	a	<0.001
Fe (mg/L)	2.06±0.12	a	1.92±0.18	a	1.83±0.07	a	1.68±0.14	a	1.02±1.77	a	0.567
Cu (mg/L)	0.55±0.1	c	0.48±0.03	c	0.29±0.08	b	0.12±0.03	a	0.08±0.04	a	<0.001
Na (mg/L)	22.75±0.59	c	20.81±0.96	bc	19.46±1.79	b	18.97±1.24	b	3.81±0.62	a	<0.001
Mg (mg/L)	96.9±1.11	c	91.03±5.11	bc	82.87±9.68	bc	79.63±1.02	b	14.13±5.38	a	<0.001
Mn (mg/L)	1.81±0.2	c	1.47±0.1	bc	1.32±0.04	b	1.26±0.04	b	0.18±0.25	a	<0.001
Zn (mg/L)	1.31±0.08	b	1.19±0.08	b	1.18±0.23	b	1.01±0.26	b	0.26±0.12	a	<0.001
(D) Cabernet Sauvignon											
pH	3.75±0.00	e	3.67±0.03	d	3.60±0.02	c	3.52±0.01	b	2.14±0.01	a	<0.001
TA (g/L H2SO4)	2.94±0.02	a	3.14±0.04	b	3.27±0.04	c	3.45±0.03	d	4.68±0.02	e	<0.001
K (mg/L)	1249.5±9.02	e	1185.23±12.76	d	1134.63±3.95	c	1044.27±24.75	b	75.77±7.94	a	<0.001
Ca (mg/L)	49.43±6.76	d	45±2.07	cd	37.87±0.91	bc	31.57±1.82	b	3.33±4.86	a	<0.001
Fe (mg/L)	3.31±0.09	b	3.24±0.27	b	3.22±0.49	b	2.65±0.15	b	0.22±0.25	a	<0.001
Cu (mg/L)	0.27±0.02	b	0.22±0.04	b	0.2±0.1	ab	0.16±0.04	ab	0.08±0.04	a	0.011
Na (mg/L)	11.33±0.58	c	9.63±0.4	b	9.43±0.35	b	8.5±0.36	b	5±0.87	a	<0.001
Mg (mg/L)	112.17±0.23	e	106.33±0.7	d	101.57±0.91	c	92.23±1.1	b	2±1.04	a	<0.001
Mn (mg/L)	1.32±0.29	b	1.18±0.32	ab	1.13±0.5	ab	0.89±0.39	ab	0.28±0.27	a	0.039
Zn (mg/L)	0.86±0	d	0.82±0.01	cd	0.78±0.02	c	0.67±0.02	b	0.03±0.04	a	<0.001

Values represent the average of three replications ± standard deviation. Rows with different letters are significantly different.

Table 3. Chemical and mineral composition of white and red wines treated with cation exchange resins in a winery setting

Wine type & composition	Percentage of wine treated with cation exchange resins as part of a blend with untreated wine (%)										
	0 (T0)		5 (T1)		10 (T2)		20 (T3)		100 (T4)		*p* value
(A) Sauvignon blanc											
pH	3.25±0.01	d	3.21±0.02	cd	3.17±0.02	c	3.05±0.03	b	2.13±0.01	a	< 0.001
TA (g/L H2SO4)	3.39±0.04	a	3.45±0.05	ab	3.52±0.04	b	3.72±0.05	c	4.44±0.04	d	< 0.001
E.C. (µS/cm)	1861.33±1.53	d	1816.67±3.51	c	1779.33±2.08	b	1714.67±5.03	a	2496.33±4.04	e	< 0.001
Tartrates (mg/100 mL of wine)	0.26±0.01	d	0.25±0.006	d	0.21±0.02	c	0.18±0.004	b	0.00±0.00	a	< 0.001
K (mg/L)	707.30±4.37	d	658.20±26.27	c	643.56±4.54	c	577.37±4.92	b	41.90±8.14	a	<0.001
Ca (mg/L)	58.60±4.87	c	57.27±3.07	bc	55.47±1.90	bc	49.90±0.78	b	1.93±0.65	a	<0.001
Fe (mg/L)	1.14±0.03	a	1.06±0.25	a	0.92±0.08	a	0.81±0.37	a	0.61±0.47	a	0.27
Cu (mg/L)	0.50±0.14	b	0.17±0.14	a	0.14±0.12	a	0.12±0.03	a	0.04±0.03	a	0.003
Na (mg/L)	12.63±0.55	d	10.17±0.72	c	8.33±0.93	bc	7.10±0.56	b	2.38±0.3	a	<0.001
Mg (mg/L)	72.20±0.10	e	69±0.35	d	64.83±0.76	c	58.73±0.64	b	0.66±0.38	a	<0.001
Mn (mg/L)	0.81±0.06	c	0.73±0.01	bc	0.36±0.31	ac	0.34±0.08	ab	0.21±0.20	a	0.005
Zn (mg/L)	0.61±0.11	c	0.51±0.01	bc	0.47±0.03	b	0.4±0.01	b	0.02±0.02	a	<0.001
(B) Chardonnay											
pH	3.7±0.01	e	3.65±0.01	d	3.58±0.01	c	3.44±0	b	2.14±0.01	a	<0.001
TA (g/L H2SO4)	3.01±0.03	a	3.14±0.02	b	3.22±0.06	b	3.45±0.03	c	4.98±0.01	d	<0.001
E.C. (µS/cm)	2520.33±2.52	d	2437.67±1.53	c	2360±5.00	b	2204±1.00	a	2592.67±7.02	e	<0.001
Tartrates (mg/100 mL of wine)	0.235±0.01	e	0.2±0.00	d	0.18±0.01	c	0.12±0.01	b	0±0	a	<0.001
K (mg/L)	1020.13±13.14	d	994.2±5.25	d	940.47±27.71	c	837.4±6.16	b	34.03±22.40	a	<0.001
Ca (mg/L)	41.46±4.82	b	37.46±3.96	b	34.93±4.55	b	31.50±5.40	b	3.13±3.31	a	<0.001
Fe (mg/L)	1.85±0.15	c	0.97±0.15	b	0.91±0.12	b	0.88±0.09	b	0.34±0.10	a	<0.001
Cu (mg/L)	0.14±0.14	a	0.08±0.07	a	0.06±0.06	a	0.07±0.02	a	0.03±0.03	a	0.511
Na (mg/L)	10.93±0.12	b	10.26±3.24	b	9.43±2.27	ab	8.73±2.97	ab	3.2±2.04	a	0,018
Mg (mg/L)	82.06±0.75	e	79.6±0.66	d	75.23±0.35	c	67.36±0.35	b	0.73±0.23	a	<0.001
Mn (mg/L)	0.7±0.05	d	0.48±0.09	c	0.33±0.07	bc	0.28±0.03	ab	0.12±0.10	a	<0.001
Zn (mg/L)	0.87±0.05	d	0.86±0.07	cd	0.76±0.02	bc	0.65±0.02	b	0.03±0.03	a	<0.001
(C) Merlot											
pH	3.65±0.02	d	3.61±0.02	d	3.53±0.03	c	3.42±0.02	b	2.026±0.05	a	<0.001
TA (g/L H2SO4)	3.31±0.07	a	3.41±0.02	ab	3.58±0.09	b	3.82±0.06	c	5.39±0.15	d	<0.001
E.C. (µS/cm)	2715.67±45.17	d	2590.33±18.34	c	2515.33±6.81	b	2348±5.29	a	2892.67±12.86	e	<0.001
Tartrates (mg/100 mL of wine)	0.31±0.01	d	0.28±0.01	d	0.23±0.01	c	0.19±0.01	b	0±0.00	a	<0.001
K (mg/L)	1136.7±102.89	c	1029.07±82.29	bc	978±34.31	bc	918.77±94.93	b	49.93±16.76	a	<0.001
Ca (mg/L)	47.73±3.45	b	45.96±1.96	b	39.37±3.98	b	40.03±8.11	b	4.9±1.55	a	<0.001
Fe (mg/L)	3.54±0.03	c	3.36±0.09	c	3.20±0.17	bc	2.97±0.19	b	0.31±0.16	a	<0.001
Cu (mg/L)	0.32±0.28	a	0.22±0.19	a	0.15±0.13	a	0.09±0.10	a	0.04±0.04	a	0.342
Na (mg/L)	9.37±0.75	b	8.77±0.45	b	8.20±0.89	b	7.20±0.66	b	2.1±2.05	a	<0.001
Mg (mg/L)	95.7±10.57	b	89.06±7.03	b	85.06±7.67	b	79.56±7.56	b	0.5±0.10	a	<0.001
Mn (mg/L)	0.83±0.08	c	0.67±0.12	bc	0.34±0.29	ab	0.33±0.11	ab	0.08±0.08	a	0.001
Zn (mg/L)	0.83±0.05	c	0.79±0.07	c	0.72±0.02	bc	0.63±0.03	b	0.11±0.01	a	<0.001
(D) Cabernet Sauvignon											
pH	3.69±0.02	d	3.65±0.02	d	3.56±0.02	c	3.42±0.01	b	2.14±0.02	a	<0.001
TA (g/L H2SO4)	3.22±0.05	a	3.34±0.06	ab	3.42±0.04	b	3.62±0.06	c	5.48±0.11	d	<0.001
E.C. (µS/cm)	2733.33±1.15	e	2634.33±6.66	c	2549.33±7.64	b	2373±2.00	a	2697.67±15.04	d	<0.001
Tartrates (mg/100 mL of wine)	0.42±0.00	d	0.41±0.00	d	0.39±0.00	c	0.32±0.01	b	0.002±0.00	a	<0.001
K (mg/L)	1040.5±118.36	b	1034.87±62.73	b	1000.7±5.01	b	867.33±61.65	b	80.33±15.80	a	<0.001
Ca (mg/L)	48.10±4.55	c	42.77±3.26	bc	39.07±2.74	b	37.2±1.15	b	4.17±2.63	a	<0.001
Fe (mg/L)	3.44±0.2	c	3.04±0.21	bc	2.95±0.18	bc	2.51±0.18	b	0.61±0.46	a	<0.001
Cu (mg/L)	0.76±0.1	b	0.34±0.3	ab	0.36±0.08	ab	0.22±0.19	a	0.05±0.05	a	0.005
Na (mg/L)	10.13±0.76	c	9.2±0.26	bc	7.93±0.55	b	7.73±0.97	b	2.17±1.07	a	<0.001
Mg (mg/L)	84.7±8.76	c	77.37±208	bc	74.70±3.76	bc	71.63±2.87	b	1.7±0.2	a	<0.001
Mn (mg/L)	0.78±0.14	d	0.61±0.03	cd	0.43±0.02	bc	0.38±0.07	b	0.09±0.08	a	<0.001
Zn (mg/L)	0.88±0.07	d	0.77±0.05	cd	0.74±0.05	bc	0.61±0.01	b	0.06±0.05	a	<0.001

Values represent the average of three replications ± standard deviation. Rows with different letters are significantly different.

(Table 3). In the case of treatment T3 (i.e., 20% of resin-treated wine), the reduction of tartrates observed varied between 23 and 48%, depending on the variety analyzed. Moreover, in all cases, the wine blended with approximately 20% of cation exchange-treated samples (by volume) showed no signs of tartrate instability after a quick cold test.

Other studies pertaining to the use of ion exchange treatments for wine stability have shown that in sherry wines, proportions between 10 and 15% of resin-treated wines were enough to achieve stability (Gomez Benítez *et al.,* 2002). Additionally, former reports have shown that resin-treated wines may have a slight negative effect on the color of red wines but without a significant influence on their sensorial evaluation (Lasanta, 2009; Mira *et al.,* 2006; Walker *et al.,* 2004).

According to laboratory-scale results, the concentration of most of the wine's metals was reduced as a result of the ion exchange treatment (Table 3). The range of metal reduction was between 16 and 76% (i.e., K in Cabernet Sauvignon and Cu in Sauvignon Blanc). In the work conducted by Benítez *et al.*, (2002), other cation exchange resins were shown to be effective in reducing the concentration of iron, copper and manganese, thus resulting in wines with a lower susceptibility to browning but with a large negative sensory impact (Benítez *et al.,* 2002).

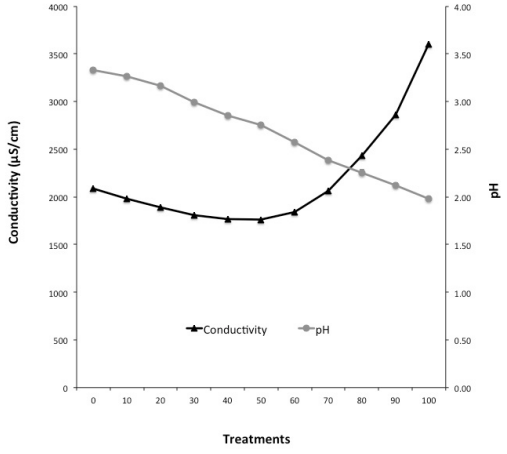

Figure 2. Variation in pH and electrical conductivity of a Chardonnay wine blended with different proportions of a cation exchange-treated product (i.e., 0 to 100% cation exchanged treated wine, replicated three times).

The observed reduction in the amount of potassium (i.e., approximately 18% reduction) and calcium (up to 24%) ions, as the proportion of resin-treated wine increased, is concomitant with a reduced risk of tartrate formation. A conjugate base of tartaric acid, namely, the bitartrate ion (HT^-), can readily react with K^+ to form potassium bitartrate (KHT), the main source of crystalline deposits found in wine during production, and a possible cause of consumer rejection (Boulton *et al.,* 2006; Waterhouse *et al.,* 2016). Calcium tartrate (CaT) is less common than KHT but generates concern among winemakers, as it is not easily removed during cold stabilization. In this case, the K content in the untreated wines was within a normal range, with average values between 700 and 1150 mg L^{-1}. As such, the average Ca content in industrial samples was between 40 and 60 mg L^{-1}, an amount below the range in which this type of instability has been observed to occur naturally (i.e., 70–100 mg L^{-1}) (Boulton *et al.,* 2006). Moreover, the lower pH of the resin-treated samples would favor the equilibrium of the protonated and monovalent forms of tartrate, instead of the divalent form (T^{2-}) required for CaT formation (Waterhouse *et al.,* 2016).

Future studies should include sensory evaluations and assessments of the effects of cation exchange treatments on the aging capacity of the treated wines. To date, there is a growing amount of evidence demonstrating the essential role that metal ions play in wine oxidation. Trace levels of transition metals, such as iron and copper, are ubiquitous in wine and have been shown to serve as catalysts of oxidation. Therefore, it seems feasible to think that a technology capable of lowering the concentration of these metals may have an effect on the rate of wine oxidation. Similarly, lowering the pH of wine could help reduce the oxidation reaction rate, improve the color expression in red wines, and help minimize the content of sulfur dioxide required for microbial activity and oxidation (Boulton *et al.,* 1996).

The main conclusions are as follows: cation exchange resins proved to be an effective tool to reduce the pH, increase the total acidity, improve the tartrate stability, and decrease the concentration of a number of cations in the treated samples. The effectiveness of the process varied according to the chemical composition of the wine to be treated and the operating conditions of the equipment.

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Resumen

F. Ponce, Y. Mirabal-Gallardo, A. Versari, y V.F. Laurie. 2018. El uso de resinas de intercambio catiónico en vinos: Efectos sobre el pH, la estabilidad tartárica, y el contenido de metales. Cien. Inv. Agr. 45(1): 82-92. El tratamiento de vinos con resinas de intercambio catiónico permite la reducción del pH, y contribuye a limitar la formación de sales de tartrato mediante el intercambio de cationes como el potasio por iones hidrógeno. Este manuscrito resume los resultados de una serie de ensayos a escala de laboratorio y bodega realizados con el objetivo de evaluar el proceso de intercambio iónico y sus efectos sobre la composición química de las muestras tratadas. Los resultados a escala de laboratorio sugieren que la magnitud de los cambios químicos producidos por las resinas varía según el protocolo de activación de las resinas utilizado, así como debido a la composición química de los vinos a tratar. De la misma forma, las pruebas a escala de bodega mostraron que los vinos tratados con resina tienen un pH significativamente más bajo, una acidez total más alta, menor formación de tartratos (medidos por peso) y una concentración reducida de la mayoría de los metales analizados. Las muestras de vino mezcladas con aproximadamente 20% de vino tratado con resinas de intercambio catriónico (en volumen) no mostraron signos de inestabilidad tartárica, usando una prueba de frío cualitativa rápida.

Palabras clave: Estabilidad tartárica, metales, pH, resinas de intercambio iónico, vino.

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