

**ORIGINAL RESEARCH ARTICLE**

# Influence of cation exchange resin-treated thermovinified red wines on the oxidative stability and colour of rosé sparkling wines produced by blending

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**ABSTRACT**

This study investigates the effect of using cation exchange resins in a red wine obtained by flash détente thermovinification on the oxidative stability of red wines and rosé sparkling wines obtained by blending the resin-treated red wine with white wine. The results show that reducing the pH of thermovinified red wines by cation exchange improves their oxidative stability and increases the intensity of the red colour, although it reduces the concentration of total anthocyanins. The analysis of metals in the wines indicates a general reduction of cations with the use of resins, which may contribute to the oxidative stability of the wines. In addition, rosé sparkling wines produced from these lower pH red wines showed greater oxidative stability over 6 months and in a forced oxidation test. These results have significant implications for the wine industry, offering new strategies to improve the production of rosé sparkling wines, which are increasingly appreciated by the market.

**KEYWORDS:** flash release, flash détente, colour evolution, oxidative stability, Alicante Bouschet, teinturier variety, CIElab



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## INTRODUCTION

Thermovinification is a pre-fermentation technique in which heat is applied to the must, resulting in a juice with an intense colour due to the rapid release of phenolic compounds from the skin into the juice (Ribéreau-Gayon *et al.*, 2021). An improvement of this technique is known as flash release or “flash détente”, where after a rapid temperature rise (around 85 °C), the must is transferred to a cooling system in a vacuum chamber, where the temperature drops rapidly, resulting in an even faster and more intense extraction and diffusion of compounds from the skins into the juice (Morata, 2019). Compared to traditional red wine vinification with skin maceration, both thermovinification techniques extract a lower amount of tannins during pressing and separation of the solids occurs immediately after treatment (Jackson, 2020). This is due to an increased extraction rate of proanthocyanidins in the presence of ethanol formed during fermentation, which makes the solution more non-polar and facilitates tannin extraction, together with the longer contact time with the solids during maceration in traditional vinification (Cerpa-Calderón and Kennedy, 2008; Hernández-Jiménez *et al.*, 2012; Morata, 2019). This low extraction of tannins can be seen as a disadvantage, for example, a red wine intended for ageing. However, in the production of sparkling wines, it can be considered an excellent condition, since excess tannins increase the astringency sensation (Ma *et al.*, 2014), which can be considered unfavourable for the palatability of the sparkling wine.

Alicante Bouschet (petit Bouschet × Grenache), obtained through controlled crossing, is considered a *teinturier* variety, being one of the few grape varieties with red pulp (Ribéreau-Gayon *et al.*, 2021). Therefore, it is generally a grape variety that is widely used in blends to add colour to wines (Revilla *et al.*, 2016). In addition, it is a variety with a complex phenolic composition, where the concentration of malvidin derivatives dominates in the skin of the berry, followed by peonidin-type anthocyanins. In the pulp of the berry there is a higher concentration of peonidin-3-*O*-monoglucoside, and red wines made from these grapes have a phenolic composition close to that of mixtures of skin and pulp anthocyanins (Muñoz *et al.*, 2009). These colour characteristics of the Alicante Bouschet variety make it a very interesting candidate for thermovinification (flash détente), since this heat treatment and subsequent pressure change have a significant effect on the cellular structure of the grape, making it possible to obtain wines with high anthocyanin content (Jackson, 2020). As a result, the volume of wine required to achieve the desired colour in blends is reduced. However, thermovinification can lead to the enrichment of the must with cations derived from the skins, which can increase the pH of the wine (Morata, 2019). Therefore, the use of cationic resins becomes interesting in this type of wine, as they can remove excess cations, lower the pH and increase the red colour intensity of anthocyanins (Ribéreau-Gayon *et al.*, 2021).

Colour plays a fundamental role in rosé wines (Peres *et al.*, 2020), where most of these products are bottled in transparent bottles. Although this type of packaging is visually appealing and serves as a marketing strategy, it can increase wine oxidation and affect the colour stability of rosé wines (Lan *et al.*, 2021; Medina-Plaza *et al.*, 2024). Rosé wine production can be achieved by various methods, such as obtaining a rosé must by direct pressing of red grapes, short maceration of red grapes, *saignée* from a traditional red wine vinification, and blending red wines with white wines (Ribéreau-Gayon *et al.*, 2021; Togo, 2018). Depending on the legislation of the country or the rules of the appellations of origin, there may be a requirement or prohibition of a specific method (Meloni *et al.*, 2019). Rosé sparkling wines are usually made from rosé wines obtained by direct pressing of red grapes or by brief maceration on the skins followed by pressing, or from blends of white and red wines (Jackson, 2020). In addition, if the region of production permits, a small amount of red wine can be added to the expedition liqueur to give the products a more vibrant and younger colour at the time of corking. This is a form of colour correction, as many anthocyanins are adsorbed by dead yeasts during fermentation (Echeverrigaray *et al.*, 2020).

Several studies have been carried out on the use of resins in wines in the last century (Esau and Amerine, 1966; Mcgarvey *et al.*, 1958), and in recent decades several studies have been carried out on cationic resins as a way of acidifying wines (Payan *et al.*, 2023). Some have dealt with the use of resins in the production of musts, white wines, and sparkling wines (Benítez *et al.*, 2002; Cisilotto *et al.*, 2019; Cisilotto *et al.*, 2020; Just-Borràs *et al.*, 2022; Mira *et al.*, 2006), red wine (Ibeas *et al.*, 2015; Lasanta *et al.*, 2013; Mislata *et al.*, 2021; Walker *et al.*, 2002), studies on resin interactions with cations in wines (Ponce *et al.*, 2018), among others (Ling *et al.*, 2024; Martínez-Pérez *et al.*, 2020; Tamasi *et al.*, 2018). However, no study to date has focused on the use of cation exchange resins in thermovinified wine and their use in blends to produce rosé sparkling wine. Red wine with a higher pH not only has a less intense colour and is more prone to oxidation (Forino *et al.*, 2020), increases the risk of microbial contamination of stored wine (Ribéreau-Gayon *et al.*, 2021). Considering the reality of many wineries, where wines intended exclusively for blending are often stored for long periods and used in small quantities for the production of both red and rosé sparkling wines in tirage liqueur or expedition liqueur, this pH reduction could improve the stability of red wine and possibly alter the characteristics of rosé sparkling wines obtained by blending white and red wines. For this reason, in this study, we propose to test whether the use of cation exchange resin in a thermovinified (flash détente) Alicante Bouschet red wine modifies the characteristics related to the colour of the red wine and the subsequent colour stability of rosé sparkling wines obtained by blending red wine with white sparkling wine.

## MATERIALS AND METHODS

### 1. Thermovinification red wine

The grape variety Alicante Bouschet (*Vitis vinifera*) was used for the experiment. The wine was produced industrially from 10,000 kg of grapes grown in *Serra Gaúcha*, Brazil. The winemaking process involved the following steps: destemming the grapes, crushing, and enzymatic treatment (3 g/hL, Everzin LCL), followed by flash détente thermovinification. Subsequently, the must was separated from the skins using a continuous press and decanter centrifuge. This was followed by flotation and fining with gelatine (20 g/hL, Gelsol). After clarifying the must, the yeast *Saccharomyces cerevisiae* (20 g/hL, Zymaflore RX60) was inoculated, and alcoholic fermentation took place at 20 °C. After alcoholic fermentation, lactic acid bacteria were inoculated for malolactic conversion (50 mg/hL, Lactoenos 450 PREAC). At the end of the vinification process, free sulfur dioxide (SO<sub>2</sub>) was adjusted to 40 mg/L using natural gas, followed by new centrifugation, cold tartaric stabilisation for 10 days (−3 °C), and tangential filtration. After these processes, the wine was stored in a stainless-steel tank, and free SO<sub>2</sub> was again adjusted to 55 mg/L. Subsequently, 40.5 L of wine were separated for the experiment.

### 2. Cation exchange resin

The cation exchange resins (pH-Stab), and sulfuric acid (ACID+) used in this study were obtained from AEB *Bioquímica Latino Americana S.A.* (BR). The cation exchange resin (pH-Stab) is a styrene-divinylbenzene copolymer matrix with sulfonic functional groups, commercialised as microspheres ranging from 0.3 to 1.2 mm. According to the manufacturer, one gram of resin can exchange 1.4 milliequivalents of H<sup>+</sup>. The dosages, application methods, washing procedures, and resin regeneration followed the manufacturer's recommendations.

### 3. Cation exchange of thermovinified wine and treatment separation

To perform the cation exchange between the red wine and the resins on a pilot scale, a cylindrical glass experimental device with a capacity of 600 mL, equipped with a valve and a porous disc filter cap to retain the resin, was used. Approximately 15.5 litres of red wine passed through the column, coming into contact with the ion exchange resin and reducing its pH from 3.8 to 2.0. From this pH of 2.0, mixtures were made with untreated wine pH 3.8 (control treatment) to produce the different treatments: pH 3.6 (13 % treated wine); pH 3.4 (25 % treated wine); pH 3.2 (37 % treated wine); pH 3.0 (50 % treated wine); and pH 2.0 (100 % treated wine), resulting in five treatments and one control. All treatments were bottled separately in 375 mL bottles. The wines were stored vertically, protected from light in a closed room at an ambient temperature of 20–22 °C, in the same light and temperature conditions.

### 4. Rosé sparkling wine obtained by blend

After 6 months of ageing the thermovinified red wines treated with cation exchange resin, rosé sparkling wines were crafted by blending red wine into the dosage liquor with white sparkling wine. The sparkling wine used was produced with base wines of the Glera (60 %) and Ugni Blanc (40 %) varieties using the Charmat method. During the bottling of the sparkling wines, bottles were separated, and the white sparkling wine received, before corking, the addition of 2 % of four different portions of red wine (wines with pH 3.8, pH 3.4, pH 3.0, and pH 2.0), resulting in four distinct treatments of rosé sparkling wines. At an experimental level, 18 bottles of rosé sparkling wine were produced for each treatment. The sparkling wines were stored vertically in boxes, shielded from light in a closed room at an ambient temperature of 20–22 °C, in the same light and temperature conditions. The sparkling wines underwent colorimetric monitoring for 6 months, with a total of 4 analyses conducted starting from time zero (0, 2, 4, and 6 months).

### 5. Analytical procedures

The pH determination was carried out using a benchtop pH meter PHS-3C (MB) (Rizzon, 2010). Reducing sugars were quantified using the modified Lane–Eynon procedure (Zoecklein *et al.*, 1990), which relies on the ability of sugars to reduce alkaline copper sulfate under specific heating conditions. The results were expressed in g/L of reducing sugars. The alcohol content (ethanol) was determined by distillation and measurement of the density of the distillate at 20 °C under hydrostatic equilibrium (Gibertini, Italy). Total acidity was determined by titration of titratable acids using NaOH solution and phenolphthalein as an indicator (Brasil, 1986), and the result was expressed in g/L of tartaric acid. Volatile acids were evaluated by steam distillation in a Super DEE apparatus (Gibertini, Italy) and quantified by titration (OIV, 2009). Volatile acidity was expressed as g/L of acetic acid. Free and total sulfur dioxide were quantified using an automatic titrator SO<sub>2</sub> Gravimeter (Gibertini, Italy) with an aqueous solution of 0.02 N iodine measured using colorimetric titration by the Ripper method (Adams, 1988). Both parameters were expressed in mg/L of sulfur dioxide.

The total polyphenol index (TPI) was determined by absorbance at 280 nm using a UV/VIS spectrophotometer T60 (PG Instruments, England) (Ribéreau-Gayon *et al.*, 2021). Tannin determination was performed by the ferric chloride (5 %) method for tannins with spectrophotometric reading at 550 nm, and the results were expressed as equivalents of tannic acid in g/L (Ribéreau-Gayon *et al.*, 1980). The concentration of anthocyanins in the samples was determined using a method that involves the discolouration of anthocyanin molecules in an acidic medium through the addition of a 15 % sodium metabisulfite solution (Ribéreau-Gayon *et al.*, 1980). This technique quantifies anthocyanins by measuring the absorbance difference before and after the discolouration process induced by the bisulfite. The reacted anthocyanins were quantified using a spectrophotometer, measuring absorbance at 520 nm.

The results were expressed in mg/L of cyanidin-3-*O*-monoglucoside equivalent.

For the determination of colour parameters of the samples, absorbance readings of the samples were taken at wavelengths of 420 nm, 520 nm, and 620 nm using a UV/VIS spectrophotometer T60 (PG Instruments, England) (Ribéreau-Gayon *et al.*, 2021). The colour intensity (CI) corresponds to the sum of absorbance readings obtained at wavelengths of 420 nm, 520 nm, and 620 nm (abs 420 + 520 + 620 nm), while the hue corresponds to the ratio between the reading obtained at the wavelength of 420 nm and that obtained at the wavelength of 520 nm (abs 420/520 nm). The brilliance of red wines (dA %) was calculated according to the following formula:  $dA (\%) = [1 - ((Abs\ 420 + Abs\ 620) / (2 * Abs\ 520)) \times 100]$  (Ribéreau-Gayon *et al.*, 2021).

The colorimetric characteristics of the wines were determined according to the OIV-MA-AS2-11 method (OIV, 2006), using the CIELab system. After centrifugation of the samples, readings were taken (using MSCV scanning software) on a UV/VIS spectrophotometer (PG Instruments T60), with a visible spectral range between 380 nm and 750 nm and a 5 nm interval between readings. Quartz cuvettes with a thickness of 1 mm were used for absorbance readings of red wines, while cuvettes with a thickness of 10 mm were used for rosé sparkling wines. To ensure comparability, all results were corrected to correspond to a 10 mm path length cuvette for both red and sparkling wines.

## 6. Analysis of Metal Cation Composition of the red wines treatments

The concentration of metal cations was determined according to the methodology of Rizzon (2010), where all the procedures for sample preparation, dilutions, and preparation of standard curves for each of the metals are specified. The alkaline earth metals, calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>), as well as transition metal ions, manganese (Mn<sup>2+</sup>), copper (Cu<sup>2+</sup>), iron (Fe<sup>2+</sup>/Fe<sup>3+</sup>), and zinc (Zn<sup>2+</sup>), were determined in the wines using a flame atomic absorption spectrometer, Analyst 100 model, by PerkinElmer (USA). Meanwhile, the determination of alkali metals such as potassium (K<sup>+</sup>) and sodium (Na<sup>+</sup>) was carried out using a flame photometer, model 910M, by Analyser (BR). The concentration of metals was expressed in mg/L.

## 7. Oxidative stability test of rosé sparkling wines

The oxidative stability test was conducted after six months of storing the sparkling wines. Samples of 250 mL sparkling wines were sealed in Winkler bottles under oxygen-free conditions. The samples were then incubated in a dark chamber at 45 °C for 10 days (Macias *et al.*, 2001). Colour analyses were performed before and after the test.

## 8. Statistical analysis

For the experiment with red wine, a completely randomised design was employed, consisting of six treatments (different pHs). In the assessment of the sparkling wines, a factorial design was adopted, incorporating four different red

wines (different pHs) into the sparkling wine, evaluated at four distinct time points. All analyses were conducted in triplicate, and the results were subjected to analysis of variance (ANOVA), followed by Tukey's test (5 %), using the statistical software SPEED Stat 3.0 (Carvalho *et al.*, 2020).

# RESULTS AND DISCUSSION

## 1. Red wine made by thermovinification

Table 1 gives an overview of the changes in the wine obtained by thermovinification due to the pH reduction obtained by mixing untreated wine (pH 3.8) with wine treated with 100 % resin (pH 2.0). These results indicate that the pH reduction obtained by mixing the wines did not affect parameters such as ethanol content, reducing sugars, volatile acidity, and tannin concentration. However, some parameters showed significant changes: total acidity increased with pH reduction, as expected with cationic resin treatment; free and total SO<sub>2</sub> decreased with pH reduction. There was an increase in absorbance at 420 and 520 nm and a decrease in colour. There was also a decrease in anthocyanin content with decreasing pH and a decrease in TPI in the 100 % resin passage treatment.

Anthocyanin colour is pH dependent and can be found in wines in different chemical structures (flavylium cation, quinoidal base, carbinol base, and chalcone) (Morata, 2019). The phenomenon of changing anthocyanin colour towards increased red intensity with decreasing pH is well described, with the red flavylium cation being the most important form at low pH (Forino *et al.*, 2020; Morata, 2019). In our study, this increase in red colour intensity (Table 1—abs 520 nm) is noteworthy, especially considering that this red wine is subsequently used to colour a white wine for the production of rosé sparkling wines. However, it is noteworthy that, together with the increase in red colour intensity caused by the pH reduction, there is a significant decrease in the total anthocyanin content of the wines as the intensity of the resin treatment increases (Table 1). The reduction in total anthocyanin content has already been demonstrated in other studies dealing with the use of cationic resins in red wines (Ibeas *et al.*, 2015; Lasanta *et al.*, 2013; Mislata *et al.*, 2021). This reduction may be due to the higher presence of anthocyanins in the form of flavylium cations in wines with lower pH (Durner, 2016; Morata, 2019), suggesting that this positively charged molecule may be adsorbed in greater quantities by the resin and exchanged for a hydrogen ion (H<sup>+</sup>), similar to other cations present in the wine. The same hypothesis is explored in a study using resin in Tempranillo red wine to justify the decrease in total anthocyanins (Mislata *et al.*, 2021).

Copigmentation alters the visual perception of most wines, enhancing their colour and resulting in wines with lower clarity and darker red hues, which visually are less evolved (Heras-Roger *et al.*, 2016). Copigmentation depends on factors such as the concentration of anthocyanins, the type and concentration of copigments, pH, temperature, and the type of solvents used (Ribéreau-Gayon *et al.*, 2021).

This makes the copigmentation equilibrium a complex phenomenon (Boulton, 2001). Copigmentation with tannins, for example, tends to increase colour intensity and stability (Gombau *et al.*, 2019). Regarding the increase in colour intensity (CI) of wines (Table 1), despite the reduction in the amount of anthocyanins and the changes in their structures caused by the lowering of pH, there may be a higher proportion of copigmented to free anthocyanins in wines with reduced pH. This copigmentation phenomenon may be related to the increase in wine colour intensity, as the copigment-to-pigment ratio has increased due to the decrease in anthocyanins.

With regard to the decrease in free and total SO<sub>2</sub> concentration, no studies were found to show that the use of cationic resins in red wine causes this effect. We believe that this fact is not directly related to the use of cationic resins, since the forms of free SO<sub>2</sub> found in wine can be molecular (uncharged SO<sub>2</sub>) and in the form of bisulfite anion (HSO<sub>3</sub><sup>-</sup>) and sulfite (SO<sub>3</sub><sup>2-</sup>) (Ribéreau-Gayon *et al.*, 2021; Waterhouse *et al.*, 2024), where theoretically none of the three forms would interact with the cationic resin. However, this decrease in sulfites could also be related to the increase in anthocyanins in the cationic form of flavylium due to the decrease in pH. Concerning this simultaneous decrease of free and total SO<sub>2</sub> and anthocyanins (Table 1), there is a significant strong positive correlation (Pearson correlation analysis = *r*) and a high coefficient of determination (*r*<sup>2</sup>), (anthocyanins

X free SO<sub>2</sub> *r* = 0.98, *p* < 0.05; *r*<sup>2</sup> = 0.96 and anthocyanins X total SO<sub>2</sub> *r* = 0.89, *p* < 0.05; *r*<sup>2</sup> = 0.79), which may support this observation to some extent. One hypothesis would be that at lower pH there is a higher fraction of anthocyanins in the form of the flavylium cation (Durner, 2016; Ribéreau-Gayon *et al.*, 2021) and a higher fraction of free SO<sub>2</sub> in the form of the bisulfite anion (HSO<sub>3</sub><sup>-</sup>) (Waterhouse *et al.*, 2024), this would increase the theoretical possibilities for these positively charged anthocyanins to combine with the bisulfite anion to form stable sulfonate adducts, increasing the fraction of combined SO<sub>2</sub> (Waterhouse *et al.*, 2024), which would explain the decrease in free SO<sub>2</sub>.

Total SO<sub>2</sub> (sum of free and combined SO<sub>2</sub>) also decreased significantly (Table 1). This is more difficult to discuss as no specific assay was performed to test this. However, in this case, based on our results, we can hypothesise that many of the anthocyanins in the flavylium cation form that were removed from the wine by ion exchange (Table 1) were already bound to a molecule of SO<sub>2</sub> (combined form of SO<sub>2</sub> with anthocyanins), thus removing the sulfite along with the anthocyanin from the wine. Another explanation for these decreases could be the higher increase in the fraction of free SO<sub>2</sub>, which is more reactive (Waterhouse *et al.*, 2024), potentially forming copigments and bonds, resulting in complex compounds that could no longer be quantified by the analytical method used in this study.

Parameter	Wines					
	3.8	3.6	3.4	3.2	3.0	2.0
pH						
Ethanol (% v/v)	11.63 ±0.42	11.60 ±0.14	11.58 ±0.05	11.55 ±0.07	11.55 ±0.07	11.54 ±0.03
Reducing sugars (g/L)	1.96 ±0.19	1.93 ±0.10	2.19 ±0.13	2.30 ±0.05	2.20 ±0.14	2.05 ±0.21
Total acidity* (g/L)	3.75 ±0.05 e	4.04 ±0.04 e	4.58 ±0.1 d	4.93 ±0.1 c	5.29 ±0.1 b	7 ±0.05 a
Volatile acidity (g/L)	0.34 ±0.03	0.33 ±0.01	0.32 ±0.00	0.31 ±0.00	0.3 ±0.0	0.3 ±0.00
Free SO <sub>2</sub> (mg/L)	53.00 ±0.70 a	46.10 ±1.41 b	34.40 ±0 c	27.70 ±0.14d	20.90 ±0.28 e	11.75 ±0.21 f
Total SO <sub>2</sub> (mg/L)	100.00 ±2.82 a	94.00 ±0.70 a	84.00 ±1.41 b	73.00 ±2.82 c	51.00 ±0 d	25.00 ±0.70 e
Abs <sub>420 nm</sub>	0.44 ±0.01 c	0.46 ±0.028 bc	0.50 ±0.035 bc	0.51 ±0.053 b	0.71 ±0.037 a	0.71 ±0.007 a
Abs <sub>520 nm</sub>	0.70 ±0.03 d	0.78 ±0.01 d	0.92 ±0.04 c	1.02 ±0.01 b	1.87 ±0.01 a	1.91 ±0.03 a
Abs <sub>620 nm</sub>	0.17 ±0.01	0.17 ±0.01	0.17 ±0.01	0.17 ±0.00	0.16 ±0.02	0.15 ±0.03
CI	1.31 ±0.03 c	1.40 ±0.14 bc	1.58 ±0.03 bc	1.70 ±0.07 b	2.74 ±0.06 a	2.77 ±0.09 a
Hue	0.62 ±0.03 a	0.59 ±0.01 a	0.56 ±0.01 a	0.50 ±0.07 ab	0.38 ±0.01 b	0.37 ±0.03 b
TPI	69.50 ±0.22 a	68.00 ±1.41 a	66.40 ±0.70 a	65.50 ±6.36 a	64.20 ±0.28 ab	59.50 ±2.82 b
Tannins (g/L)	3.50 ±0.03	3.40 ±0.11	3.30 ±0.42	3.30 ±0.14	3.20 ±0.35	3.00 ±0.21
Anthocyanins (mg/L)	795 ±5.65 a	737 ±4.24 b	610 ±0.70 c	546 ±7.77 d	493 ±1.41 e	474 ±2.82 f

**TABLE 1.** Impact of cation exchange resin treatment on general characteristics, colour, and phenolic composition of red wines.

The wines were obtained by mixing thermovinified control red wine (pH 3.8) with red wine treated with cation exchange resin (pH 2.0). The values are presented as mean ± standard deviation (n = 3). Different letters within rows indicate significant differences according to Tukey's test (*p* < 0.05). C = control; Abs = absorbance; CI = Colour Intensity (abs 420 + 520 + 620 nm); Hue = abs 420 / 520 nm; TPI = Total Polyphenol Index (abs 280 nm). \*Total acidity expressed as tartaric acid.

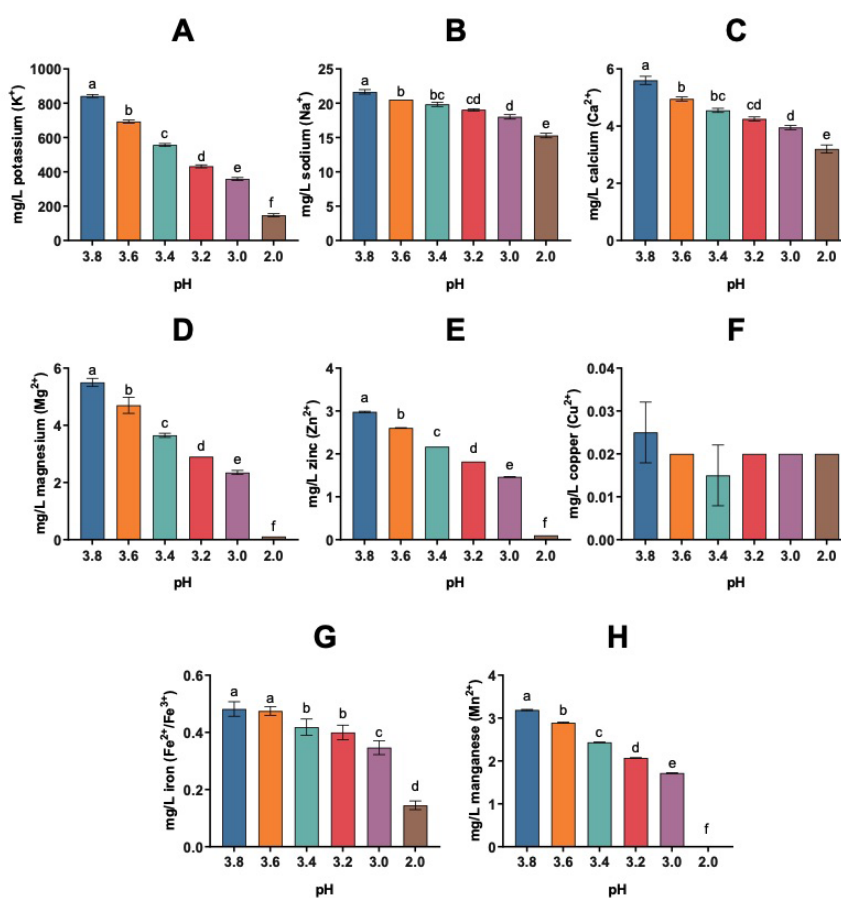
Figure 1 shows the concentration of metals analysed in wines at different pH levels. The results show an almost linear decrease with decreasing pH for almost all metals. Similar to other studies using the same resin (Cisilotto *et al.*, 2020), these analyses show that the resin used does not show selectivity between metals, interacting with almost all the cations present. Different studies with cation exchange resins also show the reduction of different types of metals in wines (Ibeas *et al.*, 2015; Mislata *et al.*, 2021; Ponce *et al.*, 2018). The lack of reduction of copper concentration in our study could be due to its already low concentration in the control wine (below 0.05 mg/L) since a significant part of the concentration of this metal decreases during fermentation due to yeast metabolism (Sun *et al.*, 2016). In addition, it is likely that the low concentration found in the control wine further reduced the possibility of ion exchange, as the theoretical encounter rate of the resin charged with  $H^+$  with  $Cu^{2+}$  was significantly reduced due to the higher concentration of other cations present. However, other metals associated with oxidative processes in wine, such as  $Fe^{2+}/Fe^{3+}$  and  $Mn^{2+}$ , showed reductions with resin treatment (Figure 1G, H). These two metals each catalyse the chemical combination of acetaldehyde with phenolic compounds and promote the formation of acetaldehyde during oxidation,

leading to higher polymerisation and later precipitation of phenolic compounds (Cacho *et al.*, 1995; Tariba, 2011). Therefore, the reduction of these metals is beneficial for the oxidative stability of the wine. Another metal that was significantly reduced was  $Zn^{2+}$  (Figure 1E). This reduction can be considered beneficial as zinc is classified as a heavy metal (Ribéreau-Gayon *et al.*, 2021).

Most of the metallic cations analysed in these studies, such as  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $K^+$ ,  $Na^+$ , and  $Ca^{2+}$  (Figure 1), are involved in various biological processes of microorganisms such as yeasts and bacteria, some of which are considered essential for their development, together with vitamins and nitrogenous compounds (Fugelsang and Edwards, 2007; Ribéreau-Gayon *et al.*, 2021). Therefore, reducing these “nutrients” in a finished wine could also improve its microbiological stability, reducing the likelihood of the development of spoilage microorganisms such as *Brettanomyces* yeasts and acetic acid bacteria.

## 2. Rosé sparkling wine obtained by blending white and red wines

The results of the analyses presented in Table 2 show the general characteristics of the sparkling wines after the



**FIGURE 1.** Metal concentrations in red wines treated with cation exchange resin.

The wines were obtained by mixing thermovinified control red wine (pH 3.8) with red wine treated with cation exchange resin (pH 2.0). Potassium (A), sodium (B), calcium (C), magnesium (D), zinc (E), copper (F), iron (G), and manganese (H). Error bars represent the standard deviation of the analyses ( $n = 3$ ). Different letters indicate significant differences between samples according to Tukey's test ( $p < 0.05$ ).

addition of red wine to the white sparkling wine at the time of bottling. No differences were observed in the sparkling wines in terms of alcohol content, total sugars, and total acidity, indicating that the addition of 2 % red wine at different pH levels does not affect these parameters. However, volatile acidity, pH, and free and total SO<sub>2</sub> showed significant differences, especially when red wines with the lowest pH values (pH 3.0 and 2.0) were added. The differences in volatile acidity can be considered subtle and of little importance. The same applies to the pH, which, although it follows a logical downward trend, remains within similar values. However, the

differences found in free and total SO<sub>2</sub> in the sparkling wines follow the same downward trend as previously observed in the red wines, with significant reductions, the lower the pH of the added wine, the greater the reduction in sulfites. These results lend some support to the hypothesis discussed previously (1. Red wine made by thermovinification) that the greater amount of anthocyanins in the flavylium cation form in wines with lower pH facilitates the combination of these anthocyanins with bisulfite and sulfite, reducing free SO<sub>2</sub> and forming stable compounds that can no longer be quantified by the analytical method used in this study to quantify sulfites.

Treatments	SW 3.8	SW 3.4	SW 3.0	SW 2.0
Ethanol (% v/v)	12.02 ±0.02	11.89 ±0.05	11.91 ±0.06	11.94 ±0.03
Reducing sugars (g/L)	12.11 ±0.12	12.06 ±0.02	11.89 ±0.12	11.66 ±0.22
Total acidity* (g/L)	5.58 ±0.1	5.62 ±0.05	5.68 ±0.04	5.94 ±0.02
Volatile acidity (g/L)	0.41 ±0.00 a	0.36 ±0.01 b	0.38 ±0.00 ab	0.42 ±0.02 a
pH	3.34 ±0.00 ab	3.35 ±0.01 a	3.32 ±0.01 ab	3.30 ±0.01 b
Free SO <sub>2</sub> (mg/L)	64.00 ±1.41 a	58.30 ±0.99 ab	51.30 ±1.83 b	32.20 ±3.11 c
Total SO <sub>2</sub> (mg/L)	142.30 ±0.99 a	136.10 ±1.27 b	126.28 ±0.03 c	121.55 ±2.05 c

**TABLE 2.** Chemical characteristics of rosé sparkling wines after the addition of 2 % of red wines treated with resin.

The values are presented as mean ± standard deviation (n = 3). Different letters within rows indicate significant differences according to Tukey's test ( $p < 0.05$ ). SW 3.8: Rosé sparkling wine with the addition of 2 % of the control red wine (pH 3.8); SW 3.4, 3.0, and 2.0 represent the rosé sparkling wine samples with the addition of 2 % of the red wine with pH 3.4, 3.0, and 2.0, respectively; \*Total acidity expressed as tartaric acid.

In the chromatic analyses of the sparkling wines over time (Table 3), the colour behaviour of the sparkling wines within the evaluated period is very similar overall. All samples showed an increase in lightness (L\*) and a decrease in chromaticity (C\*), with a loss of red colour (a\* and abs 520 nm) and an increase in yellow colour (b\* and abs 420 nm) after 6 months. There were no differences between treatments in lightness (L\*) and chromaticity (C\*). In addition,  $\Delta E$  (difference between two colours) was calculated at all analysis times using the formula  $[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$  (Spagna *et al.*, 1996), comparing all treatments with the sparkling wine sample that was added of red wine control (pH 3.8). All values were between 0 and 1, indicating an imperceptible colour difference to the human eye.

In the analyses of dA (%), where a higher value indicates a more dominant red colour in the wine, and hue, which indicates increased oxidative processes (increased ratio between yellow and red colour) (Ribéreau-Gayon *et al.*, 2021) (Table 3), differences were observed between the treatments from month 2 and month 4. There is a tendency for the sparkling wines with the addition of red wines with lower pH to have higher dA (%) and lower hue values. These results indicate that, although it may not be possible to detect differences in

the colour of the sparkling wines with the naked eye at first, the sparkling wines with the addition of 2 % red wines with a lower pH tend to have a more stable colour over time.

### 3. Oxidative stability test of rosé sparkling wine

The results of the oxidative stability test (Table 4 and Figure 2) show that the sparkling wines with the addition of wines with lower pH values maintained a greater dominance of red colour (dA (%)) and underwent less oxidation, with lower hue values. A visual assessment of the colour obtained from the CIELab coordinates (Figure 2) shows that the sparkling wine with the most stable colour after the treatment was the one with the addition of red wine at pH 3.0, which hardly changed its colour. This was followed by the pH 2.0 treatment, which had a slightly lighter colour before the test. Despite the reduction of the free and total SO<sub>2</sub> fractions in the sparkling wines with red wine addition at lower pH values (pH 3.0 and 2.0) (Table 2), the free SO<sub>2</sub> values remained relatively high (51.30 and 32.20 mg/L). The results indicate that the percentage reduction (pH 3.0 = 20 % reduction and pH 2.0 = 50 % reduction) compared to the control did not negatively affect the antioxidant activity of SO<sub>2</sub> in the sparkling wines during the 6-month follow-up period (Table 3) nor during the

Coordinates	Trat.	0 months	2 months	4 months	6 months
L*	SW 3.8	91.61 ±0.09 B	91.80 ±0.57 AB	91.91 ±0.07 AB	92.75 ±0.21 A
	SW 3.4	91.35 ±0.03 B	91.70 ±0.28 B	92.02 ±0.07 B	93.05 ±0.21 A
	SW 3.0	91.19 ±0.04 B	91.90 ±0.99 AB	92.06 ±0.12 AB	92.30 ±0.42 A
	SW 2.0	91.81 ±0.13 B	92.25 ±0.21 AB	92.35 ±0.19 AB	93.05 ±0.21 A
a*	SW 3.8	9.25 ±0.04 Ab	8.81 ±0.12 A	7.99 ± 0.09 B	7.67 ±0.09 Ba
	SW 3.4	9.61 ±0.07 Acb	8.74 ±0.04 B	8.09 ± 0.06 C	7.08 ±0.19 Dab
	SW 3.0	9.89 ±0.04 Aa	8.70 ±0.03 B	7.95 ±0.13 C	7.33 ±0.76 Cab
	SW 2.0	9.36 ±0.09 Acb	8.44 ±0.08 B	8.16 ±0.12 B	6.84 ±0.26 Cb
b*	SW 3.8	3.99 ±0.09 B	4.39 ±0.10 B	5.52 ± 0.44 A	5.52 ±0.04 Ab
	SW 3.4	4.10 ±0.21 B	4.60 ±0.05 B	5.27 ± 0.17 A	5.71 ±0.09 Aab
	SW 3.0	4.46 ±0.50 C	4.93 ±0.09 BC	5.18 ± 0.06 B	5.96 ±0.05 Aab
	SW 2.0	4.53 ±0.01 C	4.82 ±0.08 C	5.53 ± 0.05 B	6.13 ±0.10 Aa
C*	SW 3.8	12.22 ± 0.05 A	10.86 ±0.14 B	9.06 ±0.07 C	8.28 ±0.27 D
	SW 3.4	12.24 ± 0.15 A	11.07 ±0.07 B	9.32 ±0.15 C	8.61 ±0.34 D
	SW 3.0	12.53 ± 0.40 A	11.22 ±0.05 B	9.22 ±0.05 C	8.53 ±0.34 C
	SW 2.0	12.89 ± 0.04 A	11.54 ±0.16 B	9.37 ±0.03 C	8.52 ±0.61 D
h*	SW 3.8	29.63 ± 0.12 C	30.4 ±0.12 C	46.78 ±0.52 B	54.91 ±0.04 Ab
	SW 3.4	29.42 ± 0.03 C	30.95 ±0.09 C	47.12 ±1.04 B	57.61 ±1.80 Aa
	SW 3.0	29.92 ± 0.14 C	32.17 ±0.08 C	48.25 ±1.46 B	56.67 ±1.15 Aab
	SW 2.0	30.96 ± 0.04 C	32.46 ±0.03 C	48.62 ±1.59 B	57.01 ±1.59 Aab
Abs <sub>420 nm</sub>	SW 3.8	0.14 ±0.00 C	0.15 ±0.00 C	0.18 ±0.00 Ba	0.22 ±0.01 Aa
	SW 3.4	0.14 ±0.00 D	0.16 ±0.00 C	0.19 ±0.01 Ba	0.21 ±0.00 Aa
	SW 3.0	0.14 ±0.00 C	0.15 ±0.00 B	0.18 ±0.00 Aa	0.19 ±0.00 Ab
	SW 2.0	0.13 ±0.00 C	0.15 ±0.00 B	0.17 ±0.00 Ab	0.17 ±0.00 Ac
Abs <sub>520 nm</sub>	SW 3.8	0.147 ±0.00 Ab	0.146 ±0.00 Ab	0.136 ±0.00 Bab	0.131 ±0.01 B
	SW 3.4	0.151 ±0.00 Aab	0.144 ±0.00 Bb	0.130 ±0.01 Cb	0.132 ±0.00 C
	SW 3.0	0.156 ±0.00 Aa	0.153 ±0.00 Aa	0.142 ±0.00 Ba	0.132 ±0.00 C
	SW 2.0	0.154 ±0.00 Aab	0.148 ±0.00 Aab	0.141 ±0.00 Ba	0.134 ±0.00 C
CI	SW 3.8	0.31 ±0.00 Dab	0.32 ±0.00 C	0.33 ±0.00 Bab	0.37 ±0.01 Aa
	SW 3.4	0.31 ±0.00 Dab	0.33 ±0.00 C	0.34 ±0.01 Ba	0.36 ±0.00 Ab
	SW 3.0	0.32 ±0.00 Ca	0.33 ±0.00 B	0.34 ±0.01 Aa	0.35 ±0.00 Ac
	SW 2.0	0.30 ±0.00 Bb	0.32 ±0.00 A	0.33 ±0.01 Ab	0.32 ±0.00 Ad
Hue	SW 3.8	0.95 ±0.01 C	1.03 ±0.01 C	1.34 ±0.07 Bab	1.68 ±0.08 Aa
	SW 3.4	0.92 ±0.00 D	1.13 ±0.01 C	1.45 ±0.10 Ba	1.59 ±0.01 Aab
	SW 3.0	0.90 ±0.01 C	1.01 ±0.02 C	1.30 ±0.06 Bbc	1.47 ±0.04 Ab
	SW 2.0	0.85 ±0.01 C	1.02 ±0.01 B	1.19 ±0.05 Ac	1.30 ±0.01 Ac
dA (%)	SW 3.8	45.60 ±0.89 A	40.31 ±0.05 Aab	25.93 ±4.53 Bbc	9.31 ±0.01 Cc
	SW 3.4	46.72 ±0.55 A	35.67 ±0.36 Bb	19.77 ±4.93 Cc	15.26 ±0.00 Cbc
	SW 3.0	48.35 ±0.41 A	42.54 ±1.37 Aa	28.37 ±3.47 Bab	19.41 ±0.00 Cb
	SW 2.0	51.72 ±0.72 A	42.65 ±1.09 Ba	34.64 ±3.42 Ca	29.68 ±0.04 Ca

**TABLE 3.** Chromatic evolution of rosé sparkling wines during a six-month period.

The values are presented as mean ± standard deviation (n = 3). Values followed by uppercase letters in rows (across time) and lowercase letters in columns (across treatments) are significantly different by Tukey's test ( $p < 0.05$ ). SW 3.8: Rosé sparkling wine with the addition of 2 % of the control red wine (pH 3.8); SW 3.4, 3.0, and 2.0 represent the rosé sparkling wine samples with the addition of 2 % of the red wine with pH 3.4, 3.0, and 2.0, respectively; L\* = luminosity; a\* = green-red component; b\* = blue-yellow component; C\* = chromaticity; h = hue angle; Hue =  $\text{abs } 420 / 520 \text{ nm}$ ; CI =  $\text{Abs } 420 + \text{Abs } 520 + \text{abs } 620 \text{ nm}$ ; dA (%) = brilliance of red wines  $[1 - ((\text{Abs } 420 + \text{Abs } 620) / (2 * \text{Abs } 520)) \times 100]$ .

Treatments	SW 3.8	SW 3.4	SW 3.0	SW 2.0
Initial dA (%)	13.91 ±1.53 Da	23.45 ±0.23 Ca	36.33 ±1.88 Ba	39.98 ±1.31 Aa
Final dA (%)	5.88 ±1.53 Cb	8.43 ±0.23 Cb	22.42 ±1.88 Bb	31.44 ±1.31 Ab
Initial Hue	1.46 ±0.00 Aa	1.36 ±0.05 Ba	1.14 ±0.02 Ca	1.09 ±0.01 Da
Final Hue	1.75 ± 0.00 Ab	1.67 ±0.00 Bb	1.38 ±0.00 Cb	1.20 ±0.00 Cb
Δ Hue	0.29	0.31	0.24	0.11

**TABLE 4.** Chromatic result of oxidative stability test conducted with rosé sparkling wines.

The data are presented as mean ± standard deviation (n = 3). Distinct uppercase letters in the rows (indicate the difference between treatments) and lowercase letters in the columns (indicate the difference between initial and final readings of each treatment) are significantly different according to Tukey's test ( $p < 0.05$ ). Increment = difference between initial and final hue. SW 3.8: Rosé sparkling wine with the addition of 2 % of the control red wine (pH 3.8); SW 3.4, 3.0, and 2.0 represent the rosé sparkling wine samples with the addition of 2 % of the red wine with pH 3.4, 3.0 and 2.0, respectively; dA (%) = brilliance of red wines  $[1 - ((Abs\ 420 + Abs\ 620) / (2 * Abs\ 520)) \times 100]$ ; Hue =  $abs\ 420 / 520\ nm$ ; Δ Hue = Final Hue - Initial Hue.

Treatments	SW 3.8	SW 3.4	SW 3.0	SW 2.0
<b>Before test</b> <b>CIELab</b> <b>L*a*b*</b>	CIELab: 91.96 7.19 10.40	CIELab: 91.41 7.54 10.57	CIELab: 91.56 7.85 9.95	CIELab: 92.52 8.56 9.90
<b>After test</b> <b>CIELab</b> <b>L*a*b*</b>	CIELab: 93.37 6.06 11.00	CIELab: 92.41 6.53 10.39	CIELab: 91.47 7.52 9.43	CIELab: 93.17 8.16 9.28

**FIGURE 2.** Colour of sparkling wines before and after the oxidative stability test.

The sparkling wines remained in a dark chamber at 45 °C for a period of 10 days. SW 3.8: Rosé sparkling wine with the addition of 2 % of the control red wine (pH 3.8); SW 3.4, 3.0, and 2.0 represent the rosé sparkling wine samples with the addition of 2 % of the red wine with a pH of 3.4, 3.0, and 2.0, respectively; The colours of the sparkling wines presented were digitally obtained from CIELab coordinates acquired by spectrophotometer. The order of values within each colour quadrant follows the sequence L\* a\* b\*; L\* = luminosity; a\* = green–red component; b\* = blue–yellow component.

oxidative stability test (Table 4). The hue values were lower in the sparkling wines treated with wines of lower pH in both tests. In a study evaluating the oxidative stability test in red wines treated with resin (Lasanta *et al.*, 2013), it was found that the red wines whose pH was reduced showed the least increase in hue after the test.

Overall, the results obtained with the rosé sparkling wines show that, even with a small percentage of added wine, this change in the pH of the red wine also has a positive effect on the sparkling wines. Thus, in addition to increasing the longevity of the thermovinified red wine, which is better protected from oxidative and microbiological processes thanks to the increased acidity and reduced metals at a lower pH, the sparkling wines also benefit, although their pH and total acidity vary very little between the different additions. Another detail to consider is the significant reduction in SO<sub>2</sub> fractions, also in sparkling wines. This should be taken into account in winemaking practice, where it could be interesting

to carry out preliminary tests, if possible, to calculate the combination and reduction rate of sulfites for each batch of sparkling wine.

## CONCLUSION

The use of cationic resin in thermovinified red wines, to use them in blends to produce rosé sparkling wines, has proved to be an interesting technique. Despite the significant reduction in anthocyanin concentration, the red colour of the red wines intensified with the pH reduction. In addition, reducing the pH with a cationic resin improves the oxidative stability of the red wine by increasing the total acidity and removing metals associated with oxidation. The rosé sparkling wines obtained with the addition of red wines with lower pH are more stable over time, showing greater resistance to ageing and to natural and forced oxidative processes.

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