

Packaging of Wine in Aluminum Cans – A Review

Andrea Versari^{1,*}, Arianna Ricci¹, Carolina Pavez Moreno,¹
and Giuseppina P. Parpinello¹

Abstract

Background and goals

Aluminum cans represent an alternative wine packaging, offering a wide range of styles. Despite the fast-growing nature of the product category and the great market forecast, there is valid concern about the quality of wines in a can. Unfortunately, this leads to the consumer perception that these wines are low-quality products, which must be addressed by the wine industry.

Methods and key findings

Canned wines have a limited shelf life, as they often display unpleasant reductive characteristics (e.g., rotten egg and cooked vegetable off-flavors). Aluminum corrodes in the acidic pH of wine and reacts with sulfur dioxide to yield hydrogen sulfide.

Conclusions and significance

Preparing wine for canned packaging requires extra effort to understand the implications of wine redox chemistry. The wine's chemical parameters at bottling (in particular, the levels of sulfur and metals) must be managed, and the degradation of the can lining must be limited.

Key words: alternative packaging, faulty aroma, redox, sulfur compounds, wine composition

Introduction

Glass bottles still dominate the market as the most popular wine packaging (Gerini et al. 2021, Roca 2022). The use of alternative vessels is known to date back to 1917, during World War I, when the French army supplied its soldiers with wine rations in metal cans. In the mid-1930s, when technology made it possible to package food and drink on a large scale, the first canned wines arrived on the market. In 1936, the first wine in a can, a Muscatel, was offered by Acampo, a California-based winery, which was followed by a similar product from Vin-Tin-Age (Atzeni 2021).

Since 1936, several wineries have tried to can their wines, including Carina Kan-o-wine California White Port in 1954 and attempts by both Villa Bianchi Winery and Taylor California Cellars in 1979. However, since the beginning, canned wines encountered some related problems—including early appearance of turbidity in wine (maximum haze occurs at pH 3.8) (Amerine et al. 1972), degradation of the plastic liners, and corrosion of the cans themselves—which gave the wine an unpleasant, reductive, sulfur (S) smell (Duerr and Bloeck 1987, Stokes 2021) due to the reduction of sulfur dioxide (SO₂) to hydrogen sulfide (H₂S) (Amerine et al. 1972). Although the issue with aluminum (Al) clouding, which is considered to form at Al concentrations >10 mg/L, has been resolved (McKinnon et al. 1992), the issue of the S-related off-flavor persists.

The worldwide market for canned wine was valued at ~\$211.4 million in 2020, and it is likely to rise at a compound annual growth rate of 13.2% until 2028 (Grand View Research 2021). In the United States, a survey across 25 states found more than 250 winemakers and 600 wine-in-a-can products, including Sauvignon blanc, Chardonnay, Muscat, and Pinot noir (Williams et al. 2018).

Despite the fast-growing nature of the product category and the great market forecast, concerns about the quality of canned wines remain. Unfortunately, these concerns lead to a consumer perception of canned wines as low-quality and with limited shelf-life (Ruggeri et al. 2022), which must be addressed by the wine industry.

Aluminum in Wine

Total Al content in the food chain is commonly used as input to estimate the human health risk of dietary exposure for the population (Tietz et al. 2019). The European Food Safety Authority panel established a tolerable weekly intake of

¹Department of Agricultural and Food Sciences – University of Bologna, Piazza Goidanich 60, Cesena (FC) 47521 – Italy.

*Corresponding author (andrea.versari@unibo.it)

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1 mg/kg of body weight per week for all groups of people (EFSA 2013). Al in food is the result of its natural occurrence in foodstuffs, as well as its presence in additives and in materials that come in contact with food, including cans, containers, pipes, and fining agents—the latter including bentonites (Catarino et al. 2007, Bekker et al. 2019).

Al is an attractive choice for packaging beverages due to its availability, longevity, environment sustainability, versatility, high degree of barrier protection, and light weight (Deshwal and Panjagari 2020). In theory, Al in food packaging is quite resistant to corrosion because the surface quickly forms a thin layer of aluminum oxide (Al_2O_3) upon contact with oxygen. This layer protects the pure Al underneath from further oxidation and chemical attack. Nevertheless, Al is vulnerable to salty, basic, and acidic foods (including wines) that solubilize it, leading to its further release into food. Moreover, electropositive elements, such as chlorine and copper (Cu), accelerate the corrosion of electronegative Al and its alloys, which act as anodes (Soares et al. 2017). For wine packaging, including cans and screwcaps, coatings made of different materials are required on the food side to diminish Al migration. The efficacy of can linings depends on several factors, including the quality and type of material used for the cans (e.g., wrought or cast Al; pure or alloyed Al), the contact time between cans and wine, and the storage temperature. According to the Aluminum Association, the two alloys widely used in can production (3XXX Al-Mg and 5XXX Al-Mn series) have high corrosion resistance and are thus recommended for food applications (Davis 2001).

In acidic solutions ($\text{pH} < 4$) at room temperature with ionic strength values typical of wines (50 to 150 mM), Al on the can surface is present as hexahydrate ions ($\text{Al}(\text{H}_2\text{O})_6^{3+}$, usually indicated as Al^{3+}). The solubility of Al can be strongly affected by the presence of competing anion ligands such as chlorides or sulfates, as well as by carboxylic ligands such as tartaric, malic, and citric acids (Harris et al. 1996). Although the corrosion potential of Al alloys declines as the chloride ion content in the medium rises, the corrosion current density remains almost constant at $\text{pH} 3.0$ up to a chloride content of 1000 mg/kg (Soares et al. 2017). Once chloride penetrates the passivation Al_2O_3 layer, the pitting corrosion process is triggered (Kramer et al. 2018). The result of this reaction is the dissolution of Al into the wine (Figure 1).

The stability constants ($\log \beta$) of complexes between metal (M_n) and ligand (L_n) can be expressed as association constants with the following general equilibria: for $\text{M} + \text{HL} \rightleftharpoons \text{ML} + \text{H}$, $\log \beta_{1,1,1} = \log ([\text{MLH}]/[\text{M}][\text{L}][\text{H}])$, where $n(1,1,1)$ is the number of species involved. The magnitude of β is proportional to the molar concentration of the complex formed; thus, the larger the β value, the more stable the complex. Due to the large range of β values found in nature, the stability constants (also called binding or formation constants of the complex) are often expressed as logarithms. In the pH range typical of wines (3 to 4), the magnitude of the $\log \beta$ for the Al^{3+} complex with organic acids seems small for tartaric acid ($\log \beta$ for $\text{M}_2\text{L}_2\text{H}_2$ complex = 5.347 ± 0.023 ; Desroches et al. 2000) compared to citric acid ($\log \beta$ for $\text{M}_2\text{L}_2\text{H}_2$ complex

= 12.69 ± 0.011 ; Venturini and Berthon 1989) and malic acid ($\log \beta$ for $\text{M}_2\text{L}_3\text{H}_1$ complex = 12.79 ± 0.049 and $\log \beta$ for MLH_1 complex = 1.268 ± 0.049 , with constants calculated at equal molarity; Venturini-Soriano and Berthon 2001).

The effective contribution of an organic acid or metal to Al complexation depends on the actual concentration in the wine. The primary metals involved in oxidation-reduction (redox) reactions in wine are Cu (up to 6.8 mg/L), iron (Fe; up to 27.8 mg/L), manganese (Mn; up to 9.2 mg/L) (Fabjanowicz and Plotka-Wasyłka 2021), and Al, whose content is affected by wine origin, variety, and packaging. These metals can interact with the organic acids in wine (Coleman et al. 2022) to form many complexes ($\text{M}_n\text{L}_n\text{H}_n$), most of which fall into one of two categories: (i) tartrate ions with copper II (CuLH $\log \beta_{1,1,1} = 5.45 \pm 0.05$; CuL_2 $\log \beta_{1,2,0} = 4.00 \pm 0.03$; Simeon et al. 1969) and with iron III ($\text{Fe}_2\text{L}_2\text{H}_3$ $\log \beta_{2,2,3} = 9.0 \pm \text{na}$; Timberlake 1964a; and $\text{Fe}_2\text{L}_2\text{H}_3$ $\log \beta_{2,2,3} = 8.0 \pm \text{na}$; Yokoi et al. 1994) and (ii) malic ions with copper II (CuLH $\log \beta_{1,1,1} = 7.8 \pm \text{na}$ and CuL $\log \beta_{1,1,0} = 3.4 \pm \text{na}$; Būdienė et al. 2007) and with iron III ($\text{Fe}_2\text{L}_3\text{H}_2$ $\log \beta_{2,3,2} = 17.8 \pm \text{na}$; Timberlake 1964b). In addition to the stability constants, the global wine composition (including the fractions of organic acids in the 1- or 2- form at a particular pH) acts as a main determinant of the overall complexing effects (i.e., the primary species present in wine).

White wines are usually higher in malic acid than red wines, and the overall content of Al complexes seems higher in white wines (0.05 to 2.64 mg/L) than in red wines (0.11 to 0.52 mg/L) (Karaš et al. 2020). The total amount of Al in wines packaged in glass bottles varies considerably, but it provides a baseline that can be used as a logical basis for this review. In a survey of 98 French red table wines, Al content showed a log-normal distribution with average and maximum values of 0.763 and 2.550 mg/L, respectively (Larroque et al. 1994). Furthermore, Al levels in 27 wines consumed in Spain (12 red wines, 10 white still wines, and 5 white sparkling wines) ranged from 72 to 1683 mg/L, consistent with values found in wines from Germany, Italy, and Australia (Lopez et al. 1998). Additional surveys report the concentration of Al in selected wines from different countries as follows: Argentina, 0.017 to 0.018 mg/L (10 white and 10 red wines); Czech Republic, 0.132 to 1.665 mg/L (5 reds and 25 whites); Croatia, 0.515 to 1.350 mg/L (22 whites and 12 reds); Greece, 0.360 to 9.500 mg/L (15 samples); Hungary (Tokay wines), 0.010 to 1.500 mg/L (177 samples) (Tariba 2011); and Poland, 0.71 mg/L in white wines (24 samples) and 0.58 mg/L in red wines (20 samples) (Plotka-Wasyłka et al. 2018). Australian wines contain, on average, $\sim 698 \pm 596$ $\mu\text{g/L}$ Al in white wines (570 samples) and 303 ± 270 $\mu\text{g/L}$ in red wines (703 samples) (Wilkes 2018).

Although the International Office of Vine and Wine (OIV) has not established maximum Al concentration limits in wines, the accepted limit for Al in wine is 8 mg/L in Germany (Plotka-Wasyłka et al. 2018) and Australia (Wilkes 2018).

A recent study on canned red wines stored for five months showed an Al content range of 251 to 1250 mg/L (Scrimgeour et al. 2019a). An earlier study (Ferrari et al. 1992) on

250-mL Al cans showed a nonlinear migration of Al in wine over time with a maximum release at day 40 (from ~1.5 to 5 mg/L) under air storage with SO₂ (Figure 2). Furthermore, a concurrent increase in the wine's Cu content was found over time, from 0.21 to 1.21 mg/L (Ferrarini et al. 1992). The nonlinear content of Al (and its maximum release) during storage probably results from an intricate equilibrium involving changes in complexation and solubility over time, which would be impacted by a number of variables. The time course can also be variable; the specific cause-and-effect relationship needs further investigation. Regarding kinetics, a rate of 23 mg/L/day was found for canned white wine (pH 2.91, can size: 250 mL) stored at 45°C (Galassi 1985). Canned white wines (SO₂ total: 79 mg/L, SO₂ free: 4 mg/L, Cu 0.21 mg/L, Fe 2.20 mg/L) stored at either 15 or 40°C showed that the migration of Al into wine follows an inverted U-shaped curve, peaking at approximately day 40 (Ferrarini 1985).

Further model studies have confirmed that Al dissolution in wine increases with time and with a decrease in the pH of the wine (Figure 3). Al can suffer depassivation, resulting in a sharp increase in the corrosion rate when the pH value decreases below a critical value: the depassivation pH. For Al, this value is pH 3.9 (Kojima et al. 1996). A transfer rate of 0.87 mg/L/day was measured when a piece of aluminum foil (1 × 1 cm) was added to 200 mL of Riesling white wine adjusted to pH 3.8 (McKinnon et al. 1992). The effect of low pH has also been observed in soft drinks packaged in Al cans. Lemon-lime (pH 3.20) and orange (pH 2.80) soft drinks showed a regular increase in Al content over 12 months (linear regression with correlation coefficient, $r > 0.9$); the average monthly increase in Al content was 0.025 mg/L/month for the lemon-lime drink and 0.102 mg/L/month for the orange drink (Seruga et al. 1994). In canned grape juice (pH not

available), an Al migration rate of 0.18 mg/kg/month was found, with a linear increase in Al content that peaked at ~2.5 mg/kg after 365 days of storage at 35°C (Dantas et al. 2014). Canned beer (average pH ~4.0 to 4.5) also increases in Al content over time. In beers stored at 22°C, the Al content (initial value = 100 mg/L) increased at an average rate of 54 mg/L/month, peaking at ~450 mg/L after 6.5 months of storage (Ivušić et al. 2006). The kinetics of the migration of Al into the wine depends on many variables, including the levels of trace metals (e.g., Cu and Fe) commonly found in the Al alloys used to manufacture beverage cans. These metals can increase the vulnerability to pitting corrosion in the acid medium due to the formation of local galvanic micro-cells (Davis 2001), which might explain the range of values found in the literature.

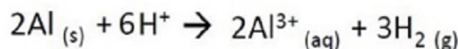
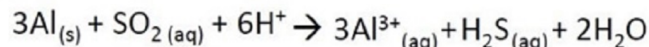
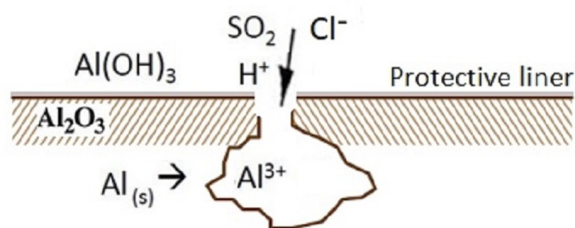


Figure 1 Schematic view of pitting corrosion of aluminum exposed to chloride ions in acidic media.

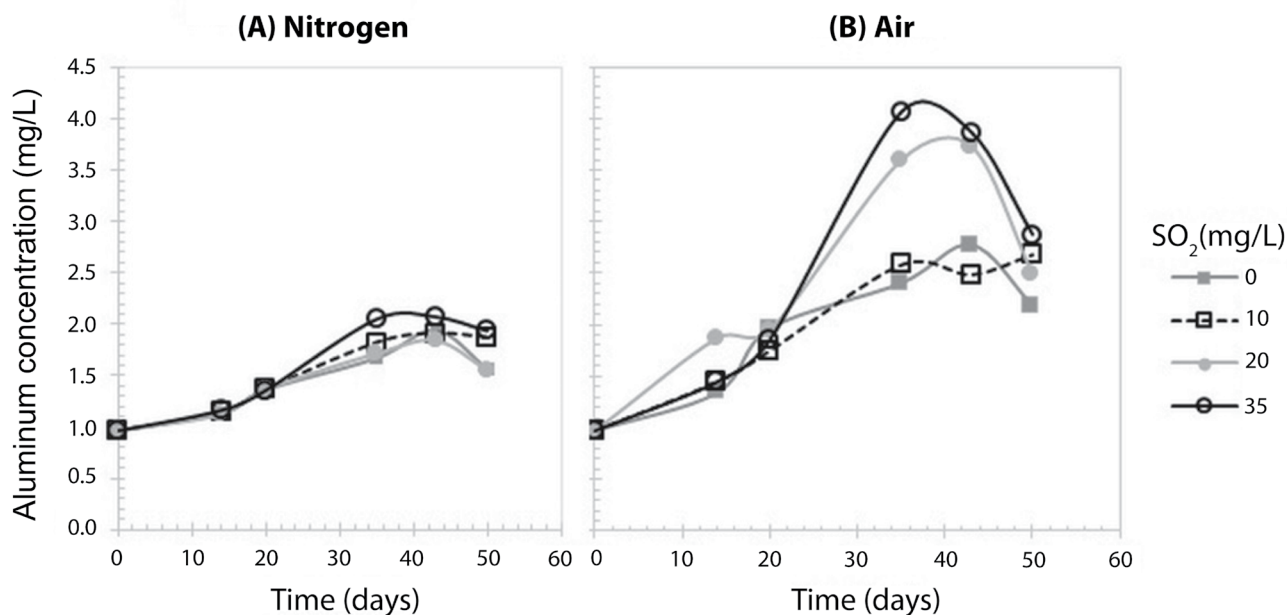


Figure 2 Variation in aluminum concentration of white wines stored in aluminum cans (250 mL) at 40°C under different headspace conditions: **A**) nitrogen and **B**) air. Each line represents free sulfur dioxide (SO₂) content: 0, 10, 20, and 35 mg/L (data from Ferrarini et al. 1992).

The relationship between organic acids and wine pH and the corresponding risk of free H₂S formation is specific to the type of wine (e.g., white, rosé, or red). The final outcome should also take into account the multiple interactions with other relevant physicochemical factors, including the type of can liner, the SO₂ content, and the presence of H₂S precursors already in the wines (e.g., Cu-bound forms of H₂S and/or polysulfanes), as described in the following sections. The origin of H₂S formation in canned wines differs from that in wine packaged in glass because Al in its elemental form reacts with SO₂ to form H₂S. However, findings from the latter scenario can provide valuable information for winemakers to reduce the risk of H₂S formation. In particular, the postbottling release of H₂S seems to be mitigated by low Cu content and low pH (Viviers et al. 2013, Clark et al. 2015, Bekker et al. 2016).

Internal Protective Coatings

Product-specific internal protective coatings should protect the metal surface from corrosion and Al migration, thereby maintaining food quality throughout storage. The topic of inner liners in canned food packaging was recently reviewed (Lestido-Cardama et al. 2022). Regrettably, there is little information in the literature on the interaction between can liners and Al in acidic beverages, including wine. Recently, this knowledge gap was investigated in a study that aimed to understand the relationship between can liners, Al migration, and H₂S in canned wines. Montgomery et al. (2023) found that wines stored in cans with epoxy liners, either with or without bisphenol A (BPA-NI), produced less H₂S (at 32 weeks: maximum and median = 51.8 and 11.8 µg/L, respectively) compared to wines stored in acrylic-lined cans

(at 8 weeks: maximum and median = 1307 and 162 µg/L, respectively). Although a correlation between two factors cannot be used as sole proof of cause and effect, it is noteworthy that H₂S development was strongly correlated with visible damage to the interior liners (Spearman's rank order test, $p < 0.001$). In the acrylic-lined cans, that damage, in accordance with H₂S production, was seen after four months of storage.

In one study, apple juice mixed with mineral water (pH 3.65) in unlined metal bottles released more Al (maximum = ~11 mg/L) than the same solution in lined bottles (maximum = ~2.8 mg/L) (Stahl et al. 2017). Unfortunately, the type of coating was not reported in the study. Furthermore, organic coatings are routinely applied to the inside (and outside) of beverage cans made of Al (Schmid and Welle 2020), usually forming thin films of 1 to 10 µm (Oldring and Nehring 2007). Although the coatings protect the metal surface, their constituents can migrate into food and beverages (Whitaker 2007, Stärker and Welle 2019). Moreover, they can reduce product volatiles by absorbing them (Wietstock et al. 2016, You and O'Keefe 2017). The chemical contamination of foods via migration from packaging represents a health risk that is usually evaluated by a specific case study of the ingredient of interest; examples include the migration of bisphenol A in canned vegetables (Nouredine El Moussawi et al. 2019) and the occurrence of several epoxy resins in canned beers (Nurlatifah and Nakata 2021). Given the need to further explore the specific interaction between coatings and metal migration, Soares et al. (2019) advanced three hypotheses to explain the complex mechanisms of Al corrosion and migration in lined cans. The porosity, thickness, and homogeneity of the coating layer all seem to play vital roles.

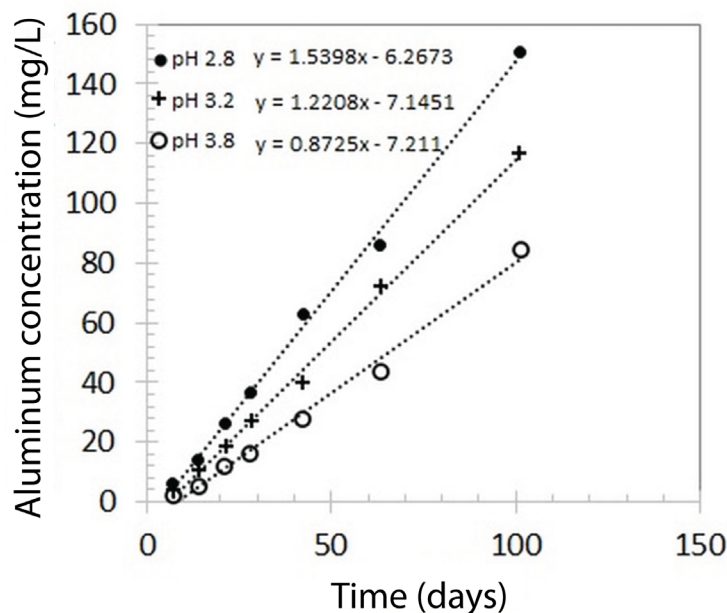


Figure 3 Migration of aluminum in white wine after adding a piece of aluminum foil (1 × 1 cm) to 200 mL of Riesling white wine with a pH adjusted to 2.8, 3.2, or 3.8 (from McKinnon et al. 1992, © 1992 American Society for Enology and Viticulture. AJEV 43:166-170 with permission).

Aluminum Corrosion and Wine Redox Chemistry

All canned foods could interact with the metal internal surface of the packaging. Even when a polymeric internal layer is added, corrosion may appear as a consequence of faulty coating. The ongoing corrosion process results in the migration of Al ions from the packaging to the beverage. The presence of pits on the metal surface represents direct evidence of the corrosion, which requires appropriate image analysis to characterize the discontinuity of the protection layer. It has been postulated that corrosion can occur via multiple mechanisms of breakdown of the protective passive oxide film (Brett 1992). In this context, localized corrosion (pitting) of the Al is a major issue in metallurgy (Reboul and Baroux 2011). Pitting corrosion—a localized cavity, hole, or pit that forms on the metal's surface—is commonly measured by counting the number and size of pits visible through a microscope within a defined surface area. Pitting corrosion of Al begins at a certain critical potential (E_p), known as the pitting potential (i.e., the lowest potential at which pitting is possible on a passive metal).

The phenomenon is usually simplified as a two-step mechanism: initiation and propagation. The initiation step of pit growth involves the breakdown of passivity, which can be driven by localized acidification due to hydrolysis of metal ions inside the pits. The propagation step involves the diffusion of the corrosion products into the bulk of the beverage. The critical pitting potential (E_p) of the AA3104 Al alloy for a citric acid solution (pH 3) is approximately < -0.45 mV (Soares et al. 2019). The Soares study (2019) evaluated concentrations similar to those found in beverages and found that the redox potential (E_h) of -0.45 mV represents the best estimate for the onset of point corrosion of aluminum in canned wines. At first, the metal ($Al_{(s)}$) oxidizes to Al_2O_3 , which forms a passive layer of protection ($4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)}$), which in the presence of water becomes (at least partially) hydroxide ($Al(OH)_3$). However, in acidic beverages (pH < 4), the Al_2O_3 layer begins to dissolve (Gayer et al. 1958), exposing the Al and advancing the corrosion process ($2Al_{(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_{2(g)}$), with the migration of metal into the bulk solution (Figure 1) and the subsequent formation of metal-complex ions (Karaš et al. 2020).

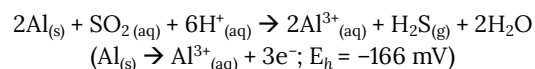
According to Ivušić et al. (2004), the Al concentration in samples of canned beer is linearly correlated with the internal pitting corrosion of the cans ($r^2 = 0.80$) and the consequent migration of this metal from the packaging to the beverage. An excess of some metals, including Al, will have a negative effect on the organoleptic properties of wine due to undesirable redox reactions.

The redox potential (E_h), determined by the ratio of oxidative to reductive components, reflects the overall balance of these components at a given time (OIV 2022). Although redox measurements in wine are only semiquantitative because the nature of every chemical species donating or receiving electrons cannot be known, redox potentials are still useful as an indirect measure of the wine's aeration status

and chemistry (Moreno and Peinado 2012). The importance of the reduction potential in wine fermentation has been known for many years (Joslyn 1949, Rankine 1963), but an advanced understanding of the role of the “mixed redox potential” in winemaking was only recently confirmed (Danilewicz et al. 2019). The authors found that the mixed redox potentials in alcoholic beverages initially depend primarily on the ethanol and O_2 content; however, when O_2 is depleted, electroactive chemical compounds (e.g., thiols and polyphenols) can greatly affect the redox measurement. These findings have implications that require further study.

The chemistry of redox reactions in winemaking plays a major role in the final quality of the wine, including the presence of a faulty reductive aroma. During alcoholic fermentation, the redox value of wine, which mostly depends on container type and O_2 management, drops to low values compatible with the occurrence of the undesirable H_2S (E_h range: -100 to -50 mV) (Killeen et al. 2018, Walker et al. 2021). In contrast, after bottling (during storage and aging at room temperature), the redox value increases depending on wine storage conditions, such as packaging and closure type (Del Álamo et al. 2006, Berović and Nemanić 2019, Sturza et al. 2021). For example, in wine at $E_h > 50$ mV, thiols (also called mercaptans) are present primarily in their oxidized forms (e.g., disulfide), thus they have less sensory influence than their reduced forms (Ferreira et al. 2018). Moreover, the positive correlation between redox potential and sensory scores for quality wines (E_0 range: 260 to 419 mV; range of sensory scores: 16.6 to 19.7 ; $r = 0.80$) and table wines (E_0 range: 280 to 414 mV; range of sensory scores: 16.0 to 17.9 ; $r = 0.69$) (Dikanović-Lučan and Palić 1992) represent preliminary indirect evidence of the possible cause-effect relationship between the two factors.

Rankine (1963) suggested that H_2S formation could be explained by a redox reaction between Al metal and SO_2 under acidic conditions:



According to Maslov-Bandic and Sacks (2019), the high corrosivity of wines in cans is mainly attributable to three factors: the low pH and high concentrations of bisulfite and Cl^- , which can compromise the integrity of the inner Al coating; the expected low rH (see below) of canned wine, which hinders the regeneration of the Al coating; and the presence of Cu^+ , which can catalyze the pitting corrosion within the can (Maslov-Bandic and Sacks 2019). The rH is the derivative of the reduction potential ($rH = -\log[pH_2]$). Thus, rH is proportional to the potential for redox, increasing as the redox reaction becomes more oxidizing and decreasing as the redox reaction becomes more reducing (Danilewicz 2012). Although rH values were used in the past, the OIV currently recommends the use of E_h values instead for measuring the redox potential of wine (OIV 2022).

Because the standard reduction potential (E_h) for the S/H_2S couple is -70 mV at pH 3.5 ($S + 2H^+ + 2e^- \rightarrow H_2S$), H_2S

formation from this source may be avoided by controlling the redox potential during wine fermentation and storage (Killeen et al. 2018, Nelson et al. 2023). Once volatile sulfur compounds (VSCs) have formed, their removal is a challenge. More specifically, at a redox potential less than -40 mV, the oxidized forms of H_2S (e.g., mercaptans, polysulfides, and polysulfanes) begin to reduce, and the reduction to H_2S is completed at a redox potential of approximately -100 mV. Thus, a variation in redox values over the range commonly found in wine simply shifts the reversible equilibria to oxidized or complexed products without removing H_2S and thiols from wine (Vela et al. 2018). The E_h -pH diagrams are widely used for aqueous solutions to show the electrochemical stability areas for the redox states of different species. The E_h -pH diagram of Cu and S highlights the coexistence of several species at wine pH (Figure 4), including Cu-S complexes (Huang 2016). Shifting from species such as H_2S and thiols to other compounds can be beneficial due to the low sensory threshold of H_2S and thiols (Goniak and Noble 1987, Siebert et al. 2010). The oxidation of H_2S and thiols is a reversible process; thus, the temporary olfactory benefit depends on several factors, including the redox value of the wine (which can be managed by controlling the O_2 content during winemaking and storage) and the role of quinone in possible thiol trapping (Smith et al. 2015). The oxidized forms of disulfides can become reduced to thiols (i.e., mercaptans) by treatment with sulfite or ascorbic acid (Müller and Rauhut 2018). The origin and fate of the many VSCs present in wine are product specific and need to be further investigated.

Actual redox values (E_h) in winemaking depend on fermentation, packaging, and storage conditions. During wine fermentation, the redox value decreases to a minimum as low as -200 mV (Kucec et al. 2002). The redox potentials of bottled Champagne wines range from a low of 100 mV (Ribéreau-Gayon et al. 2006) to 255 mV after two years, and peak at 343 mV after 11 years after tirage (Duteurtre 2016). Similar values are reported for wine in bottles with glass stoppers (162 mV) and corks (168 mV) (Clarke and Bakker 2004). A low redox potential (<40 mV) was found in Nero di Troia red wine during bottle aging (Baiano and De Gianni 2016). Canned foods are expected to have much lower redox potential due to lack of O_2 ingress. Given the lack of effective redox values in the literature for canned wines, the redox potential of canned sauerkraut ($E_{h, pH3.43} = -203$) and apple sauce ($E_{h, pH3.51} = -342$ mV) (Montville and Conway 1982) can be used to provide an estimate for canned wines. Apple sauce primarily contains malic acid (Eisele and Drake 2005), whereas sauerkraut is characterized by lactic and acetic acids (Lonergan and Lindsay 1979).

Aluminum and Sulfur Compounds Chemistry

The fate of VSCs in wine is an extensive issue that has been reviewed elsewhere (Ugliano 2013, Smith et al. 2015, Müller and Rauhut 2018, Kreitman et al. 2019, Echave et al. 2021, Ailer et al. 2022, Müller et al. 2022). A full description of the topic is beyond the scope of the current work. Although the best-known reductive compound is H_2S , additional VSCs could

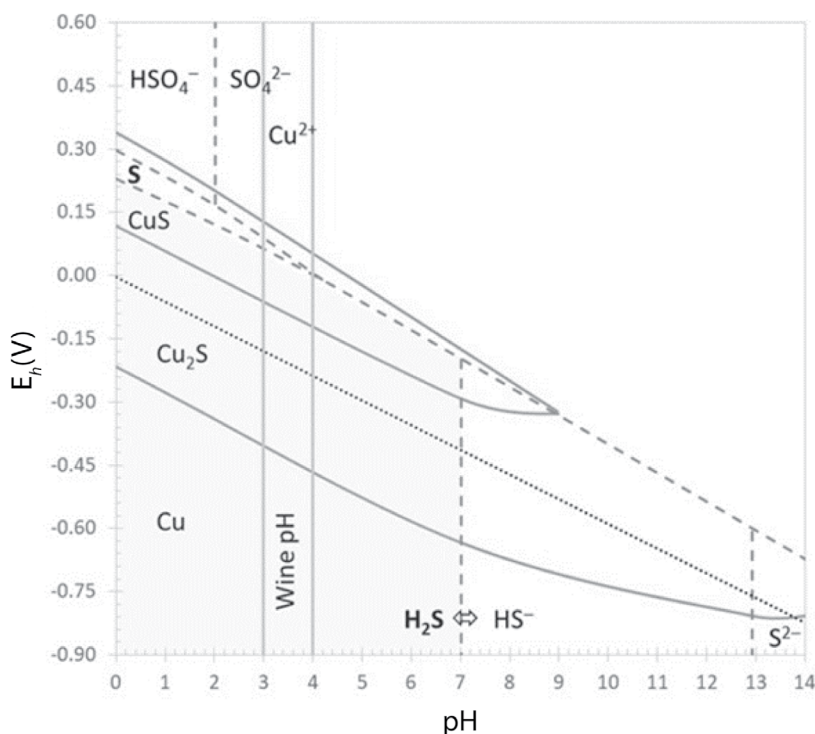


Figure 4 Redox potential (E_h)-pH diagram of Copper (Cu) (main)-sulfur (S) (ligand) (modified from Huang 2016 - *open access*).

also be responsible for the off-flavor in wines that have been kept away from O_2 . These VSCs include compounds described as “rubberlike”, including sulfides, disulfides, thioesters, and mercaptans (Scrimgeour et al. 2020). Briefly, both H_2S and methanethiol (methyl mercaptan, MeSH) are initially formed because of yeast metabolism during wine fermentation and are also formed during postbottling from the hydrolysis of precursors (Bekker et al. 2016). After bottling, the kinetics and magnitude of the chemical reactions and their impact on the sensory perception of wine during storage can be driven by O_2 exposure and temperature. In particular, canned wines aged under reductive conditions (low O_2 availability/ingress) can exhibit unpleasant odor notes such as rotten egg and boiled cabbage, mainly attributable to odor-active VSCs. These compounds are initially found in wine as Cu-sulphydryl complexes and/or their oxidized precursors, both of which have a low sensory impact; foul-smelling molecules—primarily free H_2S and MeSH—are released over time. Both compounds can be easily recognized by wine consumers due to their low odor thresholds: 1 and 2 mg/L for H_2S and MeSH, respectively (Kreitman et al. 2019).

Therefore, handling postbottling reduction in wines is critical to manage the presence of off-odors usually generated by these S compounds. Most bottled white and rosé wines—not particularly oxidized or reduced—have an average content of ~92 and 31% for H_2S and MeSH, respectively, in the form of bound S precursors (Franco-Luesma and Ferreira 2016). Glutathione is another latent source of H_2S formation in wines postbottling, especially in the presence of Cu (Ugliano 2013).

Although many VSCs are present in wine, we focus here on H_2S as the beginning form of S taints in canned wines (Figure 5). The oxide layer generally protects Al from corrosion. However, at pH <9 (as in the case of wines), the Al surface has a net positive charge, and bisulfite anions ($SO_2 + H_2O \rightarrow HSO_3^- + H^+$) can be weakly adsorbed to the internal can surface, leading to localized corrosion attack, especially where the oxide layer is defective (Šeruga et al. 1994).

Al cans provide a tight seal, letting no O_2 in, and Al migration can increase the unpleasant smell of wine. Allison et al. (2020, 2022), Allison and Sacks (2021), and Montgomery et al. (2021, 2023) validated a colorimetric method for measuring the free form of H_2S in wine. The method can be adapted for the analysis of Cu-complexed H_2S in wine by pretreating the sample with brine (Chen et al. 2017). Recent studies from Allison et al. (2020, 2022) show that when SO_2 and Al come in contact, the reaction accelerates the corrosion on the internal metal surface of the can and leads to H_2S in wine. The exact mechanism of liner failure requires further investigation. A survey on commercial canned wines found H_2S levels ranging from below the sensory threshold (~1 mg/L) up to ~46 mg/L; the sulfurous off-odor may appear as early as one month postpackaging (Scrimgeour et al. 2019b). The lack of correlation between Al content and H_2S in canned wine ($r^2 = 0.182$) suggests that several factors work together within the wine environment to drive the redox potential and the amount of VSCs (AWRI 2019). Recent evidence confirms that dissolved Al^{3+} , a common metric for characterizing corrosion, is not well correlated with H_2S formation in canned

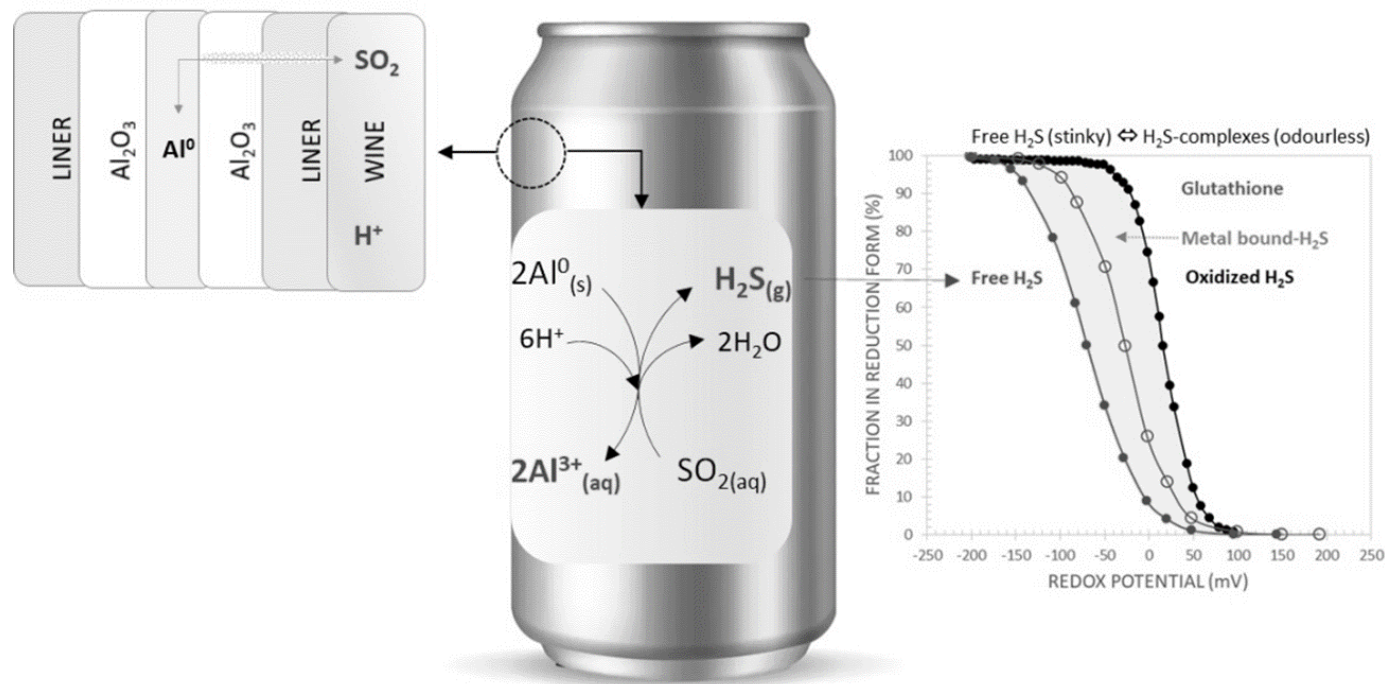


Figure 5 Overview of hydrogen sulfide (H_2S) redox chemistry of aluminum canned wine: Free H_2S (stinky) \leftrightarrow H_2S -complex (odorless).

wines, suggesting that different pathways are responsible for H₂S formation and the majority of Al³⁺ solubilization (Montgomery et al. 2021).

The level of free SO₂ in wine is dependent on pH because the molecular form of SO₂ is the microbially active form. Given the central role of SO₂ in winemaking, ~35 mg/L of free SO₂ seems to be the optimal level, balancing acceptable can corrosion levels and antimicrobial protection (Stokes and Barics 2015). As expected, in canned wine, both free SO₂ and dissolved O₂ content decline during storage due to their indirect involvement in redox reactions (Figure 6). Notably, the dissolved O₂ level of 5.5 mg/L in wine stored without inert gas (Figure 6, right plot) approximately equals the level contained in a 355 mL can with 12 mm of headspace, which is ~10 mL by volume (Allison et al. 2020).

The ratio of free SO₂ to dissolved O₂ consumption (based on mg/L) was 3.66 for canned wine with air in the headspace and 2.0 for canned wine deaerated with nitrogen prior to filling (Galassi 1985). The latter value is consistent with the mass ratios of free SO₂ to O₂ (range: ~0.9 to 2.4 with air and 1.9 to 3.1 with N₂) reported in Chardonnay wines (Waterhouse et al. 2016). Even though O₂ and SO₂ do not react with each other in wine, the theoretical total O₂-to-SO₂ molar ratio is 1:2 (1:4 as mass ratio), as SO₂ reacts with hydrogen peroxide (H₂O₂) and quinones in a wine model solution. Any departure from the ideal reaction ratio is due to a change in reactivity of SO₂ in reducing quinones back to catechols (Danilewicz 2016). Theoretically, SO₂, H₂S, and thiols can form adducts with wine quinones, with possible off-flavor outcomes. In real wines, the O₂-to-SO₂ molar reaction ratio can vary; in fact, high values are consistent with the presence of some nucleophilic compounds that may compete with bisulfite for quinones. At real wine concentrations, SO₂-quinone adducts seem favored over S nucleophiles (Bekker et al. 2016). However, decreases in the ratio were more recently attributed by

Danilewicz and Standing (2018) to the release of H₂S from intermediates in the production of sulfonic acid-substituted phenolic compounds, rather than SO₂ reducing quinones back to catechols. Managing H₂S content in wines is clearly challenging, and the role of competitive reactions is still unclear.

Moreover, at low concentrations of free SO₂ (<16 mg/L), H₂O₂ is predominantly lost through the Fenton reaction, especially in wines with a high Fe content (Elias and Waterhouse 2010). Given the problems associated with the presence of SO₂ in canned wine, it is reasonable to reduce its level while remaining aware of the implications. Some wines seem more suitable for can packaging than others; for example, some red wines seem less suited for can packaging as they develop reductive compounds (H₂S) during storage, likely as a result of the high pH, low molecular SO₂ content, and/or other complexing factors (Trela et al. 2019).

Theoretically, the production of a reductive aroma during the storage of canned wine occurs through two main pathways: the reaction of metallic Al with SO₂ (Coetzee 2021) and the decomposition of polysulfanes—which does not imply a link to Al (Bekker et al. 2018, Kreitman et al. 2019). From the thermodynamic point of view, H₂S production is favored over that of other VSCs and is therefore most relevant in canned wines (Trela et al. 2019).

The dissociation of H₂S from Cu-bound complexes in canned wine remains to be investigated (Zhang et al. 2022a). In general, the presence of Cu appears to contribute significantly to the increase in H₂S content in wine from unidentified precursor compounds. In particular, the Fe-to-Cu ratio seems to play a key role in the formation of free H₂S; in fact, a linear correlation ($r^2 = 0.9$) was found between the Fe-to-Cu ratio (for Cu levels <1.5 mg/L) and the free H₂S content six months after bottling (Viviers et al. 2014). Moreover, multivariate statistics reveal that the postbottling production of

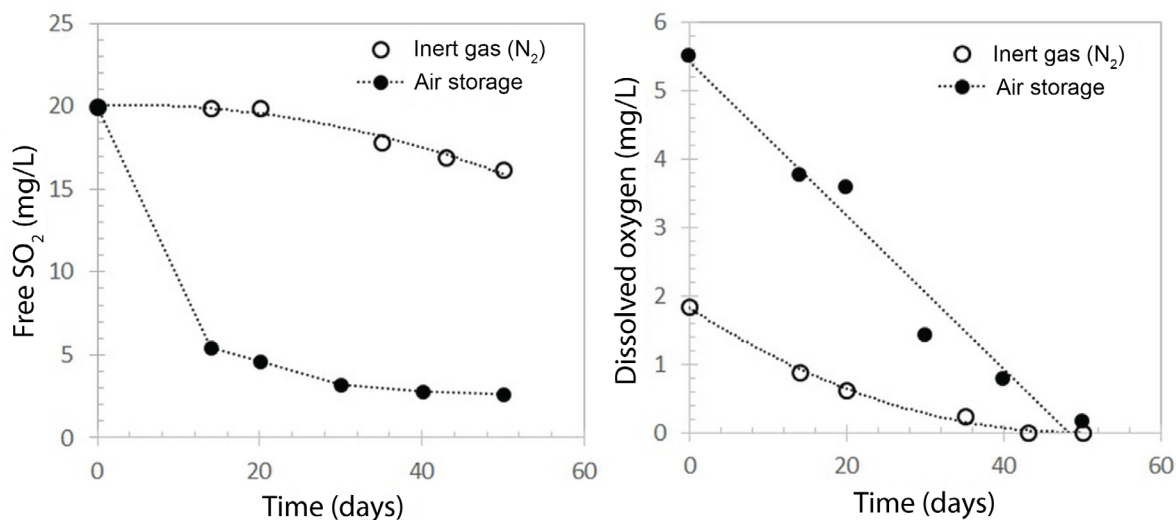


Figure 6 Change of free sulfur dioxide (SO₂) (left) and dissolved oxygen (right) in canned white wine stored at 40°C and packaged with air (●) or under nitrogen (○) (data from Ferrarini 1985).

free H₂S in Chardonnay wine was affected by several metals and combinations of metals—primarily, Zn, Al, Zn*Al, or Mn*Zn*Al (“*” indicates a combined multimetal treatment), thus underlining the critical role of Al (Viviers et al. 2013).

Conclusions: Practical Solutions to the Problem

In view of the complex and multifactorial nature of the problem, it is reasonable to assume an integrated approach is needed to identify strategies to increase the shelf life of canned wines. In canned wines, the rotten-egg aroma of H₂S is favored over the cooked-vegetable aroma of MeSH (Scrimgeour et al. 2019b) due to the low redox potential that shifts the balance of S compounds toward H₂S. Further risk factors include the pH, as well as the levels of SO₂, metals (particularly Al), O₂, and Cl in the wine. In particular, the impact of Al on H₂S content seems to be mitigated at a high total O₂ level and high pH (>3.5) together with low levels of molecular SO₂ and Cu (<0.2 mg/L).

Increasing dissolved O₂ in wines raises their redox potential and shifts the balance of S compounds toward the less odorous forms. However, the corrosion of Al gradually increases in aqueous solutions as the dissolved O₂ content increases from 0 to 4.0 mg/L (Hao et al. 2021). The control of O₂ transfer was recently addressed by the closure industry, which developed screwcaps allowing control of the O₂ transfer rate, permitting metered O₂ ingress as required. For example, the Korked spin technology uses a membrane with controlled permeability interposed between the Al capsule and the inside of the bottle, which allows the microoxygen exchange (Cappello 2015). A similar approach was patented for metal cans as well (Gatewood and Siles 2019). Obviously, even the best product packaging should be tested for each situation, taking into consideration the side effects of the redox reaction of flavonoids and ethanol on overall wine quality.

The adjustment of wine pH is a very basic practice, with the main purposes of achieving product stability and satisfying the consumer. Similarly, practical approaches to reducing SO₂ are common knowledge in winemaking (Santos et al. 2012, OIV 2020). Thus, winemakers can modify both pH and SO₂ in canned wines as needed.

Finally, another effort involves the reduction of metal content in wine before and after packaging. Levels of electrochemically labile (free) Cu >25 µg/L limit the formation of free H₂S. However, labile Cu is only a small fraction of total Cu; in commercial wines, the nonlabile form is mainly bound to organic acids and S-containing compounds (Clark et al. 2020). More recent insights have shown that the average first-order decay rate at which labile Cu is bound in wines is 0.0075 ± 0.002 after bottling (Zhang et al. 2022a). Among the several approaches to reducing metals in wine, the use of the copolymer PVI/PVP seems the most suitable (Mira et al. 2007, Vidrine 2020). PVI/PVP is a polyvinyl imidazole and polyvinyl pyrrolidone adsorbent cross-linked copolymer commonly used in winemaking as a fining agent to scavenge several metals from wine (OIV 2021). The addition of 20 to 50

g of copolymer per 100 L of wine will generally remove most of the Cu and H₂S complexes in white wines, minimizing the risk of the latent development of reductive aroma due to H₂S release from metal complexes (Zhang et al. 2021). Together with metal-removing fining agents, the use of a suitable filtration system can further decrease the risk of latent H₂S release from Cu-H₂S complexes. Diatomaceous earth with depth filtration has been shown to be a more effective filtration system than a polyethersulfone membrane for the removal of 50 to 97% of sulfide-bound forms of Cu (Cu fraction III) (Zhang et al. 2022b). However, further work is required to scale up these preliminary findings and develop practices based on an individual wine's composition and style. Regarding Al, the next generation of cans should use improved cross-linked polymers to reduce Al migration during wine storage. Thus, there is a need to conduct new studies with a transdisciplinary approach to understand the specific interactions between product and container, the technological peculiarities of the canning process, and the physicochemical and sensory complexities of canned wine during storage.

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ORCID

Andrea Versari 0000-0003-2960-0619

Arianna Ricci 0000-0002-4810-9123

Giuseppina Paola Parpinello 0000-0002-1439-8035

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