



RESEARCH FOCUS

The Chemistry of Canned Wines

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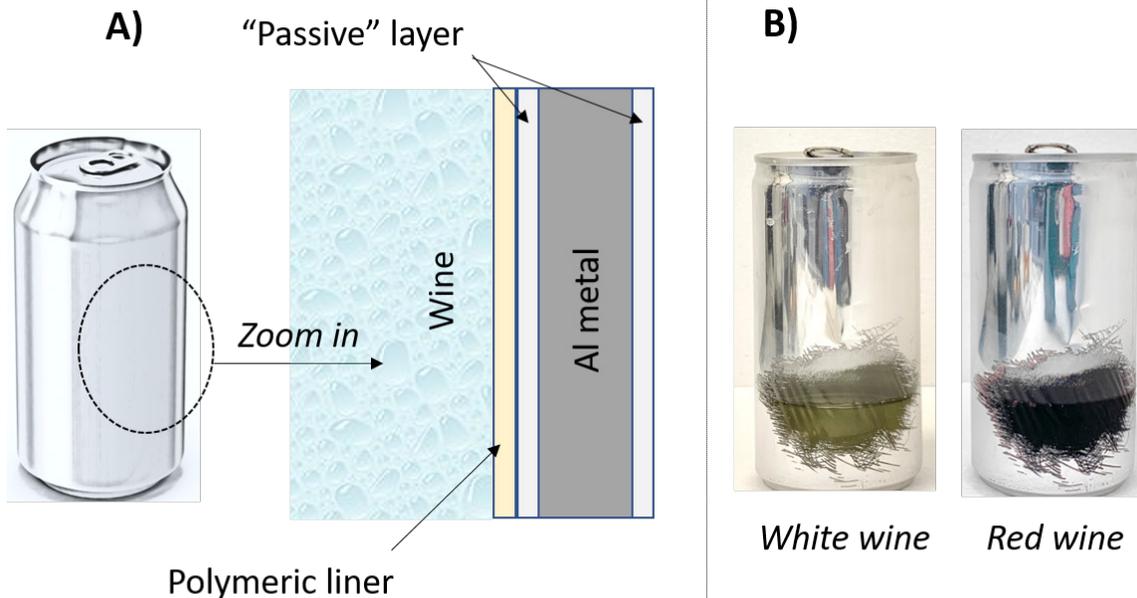


Wine in cans is an increasingly popular alternative packaging option but some producers report occasional issues with shelf stability and quality degradation.

Wines packaged in aluminum beverage cans are gaining in popularity with a 30-fold increase in sales since 2012. However, producers are concerned that canned wines occasionally develop hydrogen sulfide (H₂S, "rotten egg" off-odor) off-aromas during storage. Here we review the potential sources of chemical and physical interactions of wine with polymer-lined aluminum cans that could affect shelf life and sensory attributes. Preliminary data from our group and others indicate that SO₂ may circumvent the interior can liner in some wines and the subsequent reaction of SO₂ with aluminum leads to H₂S. Future research directions are suggested for improving our understanding of why certain wines are more susceptible to H₂S formation during can storage.

KEY CONCEPTS

- Sales of wine in aluminum beverage cans have grown over 30-fold in the period 2012-18 due to considerable advantages in their consumer appeal, light weight, strength, and recyclability.
- There has been little work on the impact of cans on wine chemistry. In general, the negative interactions between packaging and beverage can be classified as either Flavor Degradation, Scalping, or Tainting.
- Aluminum cans have a thin interior polymeric coating (also called a "liner" or "lacquer") to protect the aluminum from the beverage.
- Flavor degradation and scalping (loss of compounds associated with sensory attributes), are likely of low concern in canned wine due to low risk of oxidation and negligible scalping of non-polar compounds by the can liner.
- Development of H₂S ("rotten egg" aroma) is reported to occur in some canned wines. This is likely due to reaction of SO₂ with the aluminum, as opposed to release of H₂S from other precursors.
- Opportunities exist for further extending the shelf life wine of wine in cans by focusing on the interaction of SO₂ and the can liner.



Note: Not to scale!

Figure 1. (A) Anatomy of an aluminum beverage can. The body and lid are formed from aluminum alloys. The aluminum metal surface rapidly and spontaneously oxidizes in the presence of O₂ and/or H₂O to produce a less reactive ‘passive layer’ of aluminum oxide or other oxidized forms. The beverage can interior is then coated with a 1-10 μm polymeric liner to protect the passive layer from beverage components. (B) Aluminum wine cans with portions of the metal dissolved in caustic solution to reveal the transparent interior liner.

Background

Wines in aluminum beverage cans are one of the fastest growing sectors in the wine industry. From a packaging standpoint, canned wines have several advantages. Beyond having strong consumer appeal, lower shipping costs, and excellent recyclability, they are also excellent oxygen barriers especially compared to other lightweight plastic packaging.

However, winemakers and the patent literature have reported that canned wines will occasionally develop hydrogen sulfide (H₂S, “rotten egg” aroma) after several months of storage. Similar outcomes have been seen in some canned hard ciders.

Preliminary work in our lab, along with the existing literature, suggests that this H₂S formation is likely due to reaction of SO₂ with the aluminum. This observation is surprising, as it indicates that SO₂ may circumvent the interior can liner in certain wines.

This report will review what is known about the chemistry of wine in cans, including what is known about the interaction of SO₂ and aluminum beverage cans, and discuss future areas for research.

Canned wine: Moving fast and not breaking things.

Commercial examples of wine in metal cans dates to attempts with tinsplate steel in the 1930s (Pinney 1989), but the modern history of wine in aluminum beverage cans dates only to the last two decades (Williams et al. 2019). In the US, the value of wines packaged in aluminum cans grew from \$2 million in 2012 to \$69 million in 2018 (Weed 2019).

The appeal of canned wines has several explanations (Williams et al. 2018). For consumers, cans are more convenient than conventional 750 mL glass packaging – no corkscrews are required, single portion (187 mL, 250 mL) or double portion (375 mL) packaging is common, and consumers don’t have to worry about broken glass at pools, concerts, or backpacking trips. Cans also lend themselves to distinctive designs and are less expensive to ship due to their light weight and ruggedness. Finally, from an environmental perspective, wine in cans are an attractive alternative to glass or plastic packaging like bag-in-box, due the well-established domestic recycling stream for aluminum.

The challenges of packaging wines in cans – especially in contrast to packaging in glass bottles – have been recently reported (Lasky 2019; Williams et al. 2018). These articles highlight important considerations surrounding logistical aspects of canning wines (e.g. label design, headspace and fill level control, can sizes), yet only briefly mention the importance of wine chemistry in determining the shelf life of a canned wine. Here, we summarize our state of knowledge regarding the chemistry of wine in cans, and identify opportunities and needs for future research.

What is an aluminum beverage can?

A cartoon depiction of an aluminum beverage can cross-section is shown in **Figure 1a**. Bare aluminum metal is highly reactive but will also rapidly form a very thin (nanometer scale) passive layer of alumina oxide when exposed to air or water (Vargel 2004). The low reactivity

of the *passive layer* is the reason why aluminum foil and other common aluminum-based materials are relatively inert.

Even with the passive layer, exposed aluminum will corrode slowly in acidic media. Therefore, the can interior must be protected from direct contact with wine and other low pH beverages by coating it with a thin layer (typically 1-10 μm) of a polymer, referred to as a *coating, liner or lacquer* (Robertson 2005). The liner is typically invisible to the consumer but can be seen by chemically etching away the outer aluminum layer (e.g. by dissolving it in a caustic solution, see **Figure 1b**).

From this perspective, an aluminum can is better thought of as a plastic bottle, with an aluminum can surrounding the bottle for mechanical support – however, the plastic liner of a can is about 1/100th the thickness of a typical plastic bottle, and thus creates much less waste.

Can liners are considered food contact substances, and their composition must be approved by the FDA (Geueke 2016). In the US, most beverage can liners were historically composed of bisphenol A (BPA) based epoxy resins. However, due to the introduction of California's Prop 65, which requires the labeling of BPA-based packaging materials as suspected endocrine disruptors, many producers are utilizing alternative liner materials, including non-BPA epoxies, acrylic and polyester (Bomgardner 2019).

Finally, cans are not produced from pure aluminum, but rather from *alloys* of aluminum mixed with small amounts of other metals. For example, can bodies are usually produced from aluminum alloy 3004, which contains ~1% each of Mn and Mg (Vargel 2004). The use of alloy improves the formability and strength of the metal for the rolling and extrusion steps necessary for can body production, as well increasing resistance to corrosion (Vargel 2004).

The three demons of storage: Degradation, scalping, tainting.

In the absence of microbial spoilage, the detrimental sensory changes that occur during the shelf storage of foods and beverages can be classified as either flavor degradation, scalping, or tainting (Duncan and Webster 2009).

Degradation refers to ordinary chemical processes that occur during product storage that result in a loss of quality. For example, bread becomes stale as moisture is lost. In the case of wine, the most important source of flavor degradation is typically oxidation. To slow oxidation, most table wines are packaged with 20-40 mg/L free sulfur dioxide (SO_2) to limit the effects of oxidation. Exposure of wines to oxygen results in formation of oxidation products (quinones and hydrogen peroxide), which will react with total sulfur dioxide (SO_2) at a ratio of 4:1 on a weight-by-weight basis.

Oxidized aromas, brown color formation and other signs of quality deterioration are reported to start appearing at free $\text{SO}_2 < 10$ mg/L. Oxygen introduced during or after

the packaging step may arise from several sources: oxygen initially present in the wine or headspace (also called total package oxygen, TPO), external diffusion from the environment, and diffusion from the packaging material (Lopes et al. 2007).

i) O_2 may ingress into the package from the external environment.

In a sound aluminum can with a well-formed double seam, external oxygen ingress should be negligible. Although no data exist for ingress into canned wine, research on 12-oz (355 mL) beer cans reported 0.04 mL of air ingress over a 12-week period (Wisk and Siebert 1987). This equates to 0.1 mg O_2 /L per year, comparable of less than what has been reported for wines stored in glass bottles under screwcaps (Dimkou et al. 2011). Using the 4:1 ratio described above, this amount of O_2 would result in the loss of 0.4 mg SO_2 /L per year. Considering that most canned wines are consumed within a year of release, this amount of SO_2 loss is unlikely to affect quality.

ii) O_2 may diffuse from the packaging materials into the wine.

This effect can be important to traditional cork-finished wines due to the presence of voids in the cork. However, even for a relatively thick can liner (10 μm) and an implausibly high void percentage (10%) the can liner could contain only trace amounts of O_2 (<1 mg per can). Thus, diffusion of O_2 from the can materials is likely to be negligible.

iii) O_2 may be present in the headspace or dissolved in the wine at the time of packaging.

The beer industry standard for fill height of a 355 mL (12 oz) can is 12 mm of headspace, which equates to about 10 mL. If this headspace is composed entirely of air, the oxygen present in this headspace of 375 mL can (~5 mg O_2 /L) would be enough to consume 20 mg/L of SO_2 (!). During canning of beer and sparkling wines, this headspace oxygen is largely limited by the CO_2 gas expelled following filling, and in still wines can be controlled with inert gases like nitrogen. Canning operators typically target < 1 mg/L total package oxygen (TPO) for 375 mL cans, which would result in a loss of 4 mg/L SO_2 .

In the authors' experiences, SO_2 in canned wine will decrease in the 2-4 weeks following canning as oxygen present at packaging is consumed, after which total SO_2 typically decreases <5 mg/L over the subsequent year. Although this indicates that SO_2 loss due to reaction with the can liner or ingressing O_2 is negligible, we have occasionally worked with winemakers who have observed dramatic losses of SO_2 in canned wines (up to 70 mg/L over several months) during long-term storage for unknown reasons. Potentially, this SO_2 loss could be due to its reaction with the can liner, although further investigation is warranted.

Scalping refers to the loss of compounds from a food or beverage by its migration into the packaging material. Typically, the compounds of greatest concern for scalping are non-polar flavors and odorants, which can be absorbed into non-polar polymer packaging materials.

Scalping has not been studied in canned wine but has been studied with hop constituents in canned beer. Witstock et al. (2016) reported significant scalping only for highly non-polar odorants, like limonene. Similar observations have been made for wines stored in the presence of other polymeric packaging materials, such as synthetic corks (Capone et al. 2003), although these would have much greater absorptive volumes than can liners.

Although limonene is found in sub-sensory thresholds in wine, there are other odorants with similar or greater log P values to limonene (approximate log P of 4)¹. Using log P > 4 as a criterion, the impact odorants in wine at risk for scalping in wine include:

- 1,1,6-trimethyldihydronaphthalene (TDN, “petrol” odor of aged Riesling)
- Rotundone (“black pepper” odor of Syrah and other varietal wines)
- 2,4,6-trichloroanisole (TCA, “cork taint”) and related haloanisoles.

Presumably, winemakers would not be opposed to the scalping of TCA from their wines, if present! Many other important wine odorants like linalool/geraniol, most esters, oak-derived volatiles, and volatile thiols have log P values < 4 and their scalping is expected to be negligible in canned wines.

Tainting refers to introduction of undesirable flavor compounds into the food or beverage due to the packaging. Often, tainting is due to the migration of odorants from the packaging into the product, as can occur in the well-known phenomenon of TCA introduction from contaminated corks.

A less common type of tainting involves the reaction of foodstuff components with the packaging to produce tainting compounds. For example, coatings on steel food cans may contain trace amounts of mesityl oxide impurities, which can react with hydrogen sulfide (H₂S) naturally present in foods to generate the potent 4-mercapto-4-methyl-pentan-2-one (4-MMP, “catty taint”) (Mottram 1998). These types of taints (which we will refer to as “secondary taints”) are more challenging to predict because they will form only with certain combinations of foods (or beverages) and packaging materials, and therefore may be overlooked during initial testing with simple model systems like water.

H₂S-associated off aromas.

In canned wine, an occasional but important taint appears to be a “rotten egg, reduced” odor brought about by H₂S. H₂S has a sensory threshold of around 1 µg/L (1 ppb) in wine (Siebert et al. 2009), and is most often experienced by winemakers during fermentation as a byproduct of yeast metabolism. The formation of H₂S during storage

¹ Log P is a measure of the relative solubility of a compound in water vs. a non-polar solvent. A higher log P indicates a more non-polar compound

of wines in aluminum cans has not yet been described in peer-reviewed papers, but has been reported in multiple patents (Daiwa 2006; Stokes and Barics 2014), and more recently at conferences (Maslov-Bandic and Sacks 2019; Trela 2019; Trela et al. 2019).

In these reports and in conversations with winemakers, the time necessary to form detectable H₂S or reduced aromas can vary considerably among both wines and can types – many canned wines experience no issues after a year of storage, while others develop detectable H₂S within several months. Importantly, the existing reports all point to SO₂ as a likely source of H₂S, thus tainting presents a potential technical challenge to canned wine quality.

SO₂ as an H₂S precursor: Not the usual H₂S-uspect.

The phenomenon of wines developing sulfurous off-aromas (also called “reduced” aromas) during anoxic storage has been well reported in recent years.

At the International Wine Challenge in London, a competition that draws over 10,000 entries from prestigious wineries from around the world, reductive off-aromas accounted for 25-30% of all reported wine faults, comparable to the incidence of cork taint and oxidation (Goode and Harrop 2008).

A survey of commercial wines with reduced aromas reported that H₂S was the volatile sulfur compound most often found in excess of its sensory threshold (Siebert et al. 2010). Several latent precursors of H₂S in finished wine have been identified, including copper sulfide complexes (Cu_xS_y) and organopolysulfanes (RS-S_x-SR') (Kreitman et al. 2019).

Could these same H₂S precursors be responsible for forming H₂S in canned wines, too? As mentioned above, cans allow less oxygen ingress than screwcaps, and the resulting anoxic environment will certainly favor formation and preservation of H₂S from any precursors in the wine. However, the anoxic environment appears to be only a partial explanation for the incidence of H₂S in canned wines.

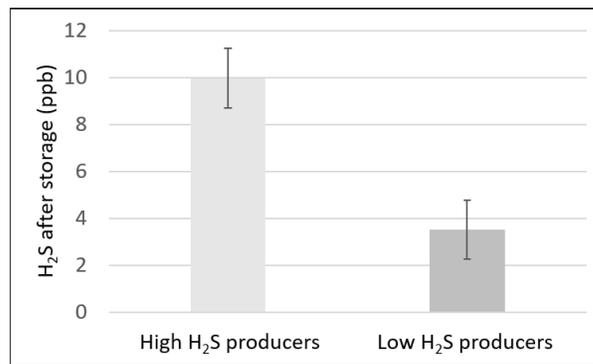


Figure 2. H₂S formed in model wine (pH 3.5, 50 mg/L free SO₂, 12% EtOH) following 2 weeks of storage at room temperature. Cans were classified as high or low H₂S producers (n=4 for each) based on previous observations with commercial wines. No H₂S was observed in model wines without SO₂.

Anecdotally, winemakers have reported that wines stored in aluminum cans are more likely to produce detectable H₂S than the same wines stored under screwcap. Beyond this, *there are other pieces of evidence that point to SO₂ as a key source of H₂S during canned wine storage.*

- Model wines consisting of SO₂ in hydroalcoholic solution will produce detectable H₂S within weeks when stored in commercial, lined aluminum cans (**Figure 2**), even though they lack any wine-derived latent H₂S precursors.
- Real wines (as well as model SO₂ containing solutions) will rapidly generate H₂S when exposed to aluminum and its alloys. Formation of H₂S is reported to increase in dose-dependent manner with increasing SO₂.²

With respect to this second point, the observation that wines will generate H₂S when brought into contact with aluminum alloys dates back over 80 years (Mrak et al. 1937)³. The noted enologist Bryan Rankine later reported that both wine and SO₂ solutions would produce H₂S when they are exposed to aluminum surfaces (Rankine 1983). Rankine, along with others (Daiwa 2006; Trela et al. 2019), hypothesized that H₂S formation could be explained by a redox reaction between aluminum and SO₂ under acidic conditions:



This reaction is thermodynamically favorable at wine pH.

In our own experience, we observed production of > 10 µg/L H₂S (well in excess of sensory threshold) after incubating an aluminum coupon in a 500 mg/L SO₂ solution for a couple of days at room temperature. At neutral pH, we observe white, pustule-like blisters of aluminum hydroxide on the aluminum surface (**Figure 2**). The blisters are not visible in wine, possibly because they dissolve at wine pH, but will sometimes be observed in the headspace of the can. H₂ (from reduction of H⁺) is also expected to be formed (Vargel 2004). These conditions are extreme compared to what would be observed in a lined can with a typical wine, where H₂S is expected to take months to be detected.

The importance of SO₂ is appreciated by can manufacturers, who provide recommendations for maximum free SO₂ at packaging (e.g., <35 mg/L) (Stokes and Barics 2014).

What about the liner? Shouldn't that stop SO₂?

In principle, the polymer liner is supposed to prevent contact between the beverage and the metal surface. However, as mentioned earlier, neutral compounds can diffuse into and through components of packaging, a phenomenon responsible for “flavor scalping” of odorants. Volatile substances like molecular SO₂ are also reported to be able diffuse through coatings and accelerate corrosion in industrial settings (Özcan et al. 2002).

In a 2006 patent, Daiwa Corp proposed that molecular SO₂ diffuses through the liner material to reach the passive layer (Daiwa 2006). An alternative mechanism could involve imperfections (pores) in liner material which allow free SO₂ (primarily in the form of bisulfite) to reach the metal surface.

With either diffusion of molecular SO₂ through the liner, or passage of free SO₂ through pores, we expect the liner to have a strong effect on performance. In our lab, we have observed considerable variation in H₂S produced during storage of model wines in cans with different liners (**Figure 3**).

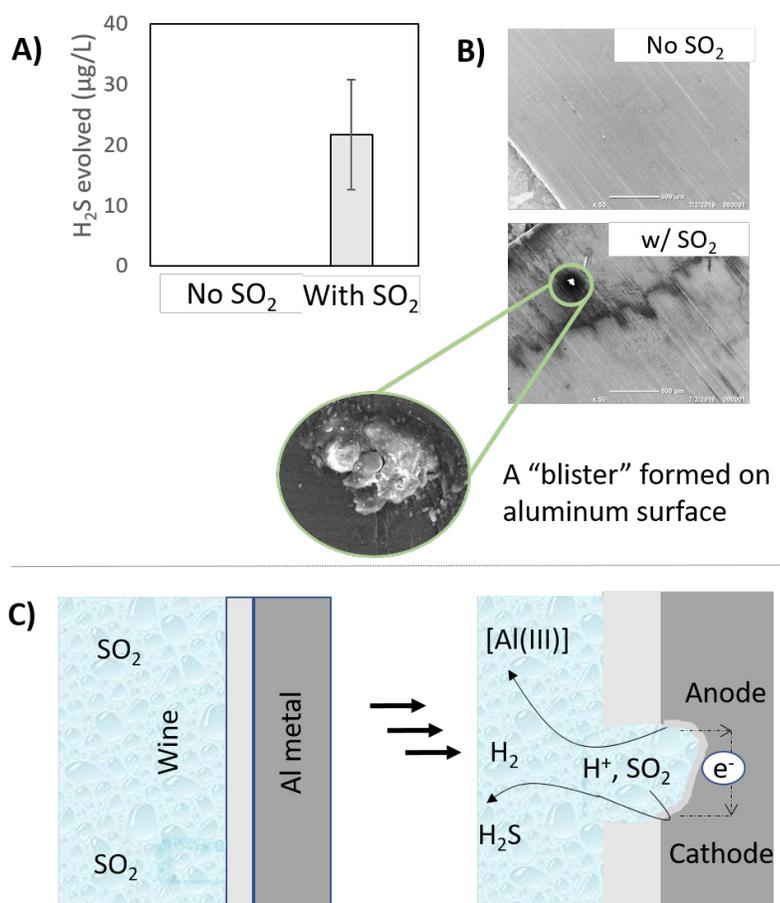


Figure 3. (A) H₂S production following incubation of aluminum coupon in aqueous ethanol solutions w/ or w/o SO₂. (B) Scanning electron microscope (SEM) images of pit and “blister” on aluminum surface following exposure to SO₂ from previous experiment. (C) Cartoon of hypothesized redox reaction between SO₂ and aluminum, leading to H₂S and pitting corrosion.

² An additional piece of circumstantial evidence is that canned beer (which usually has no added SO₂) is not reported to develop H₂S during storage, but canned cider (which does have added SO₂) will occasionally develop H₂S.

³ The paper lists Lyman Cash as a middle author. Mr. Cash was a long-time enologist for E&J Gallo and is best known for his eponymous still for measurement of volatile acidity.

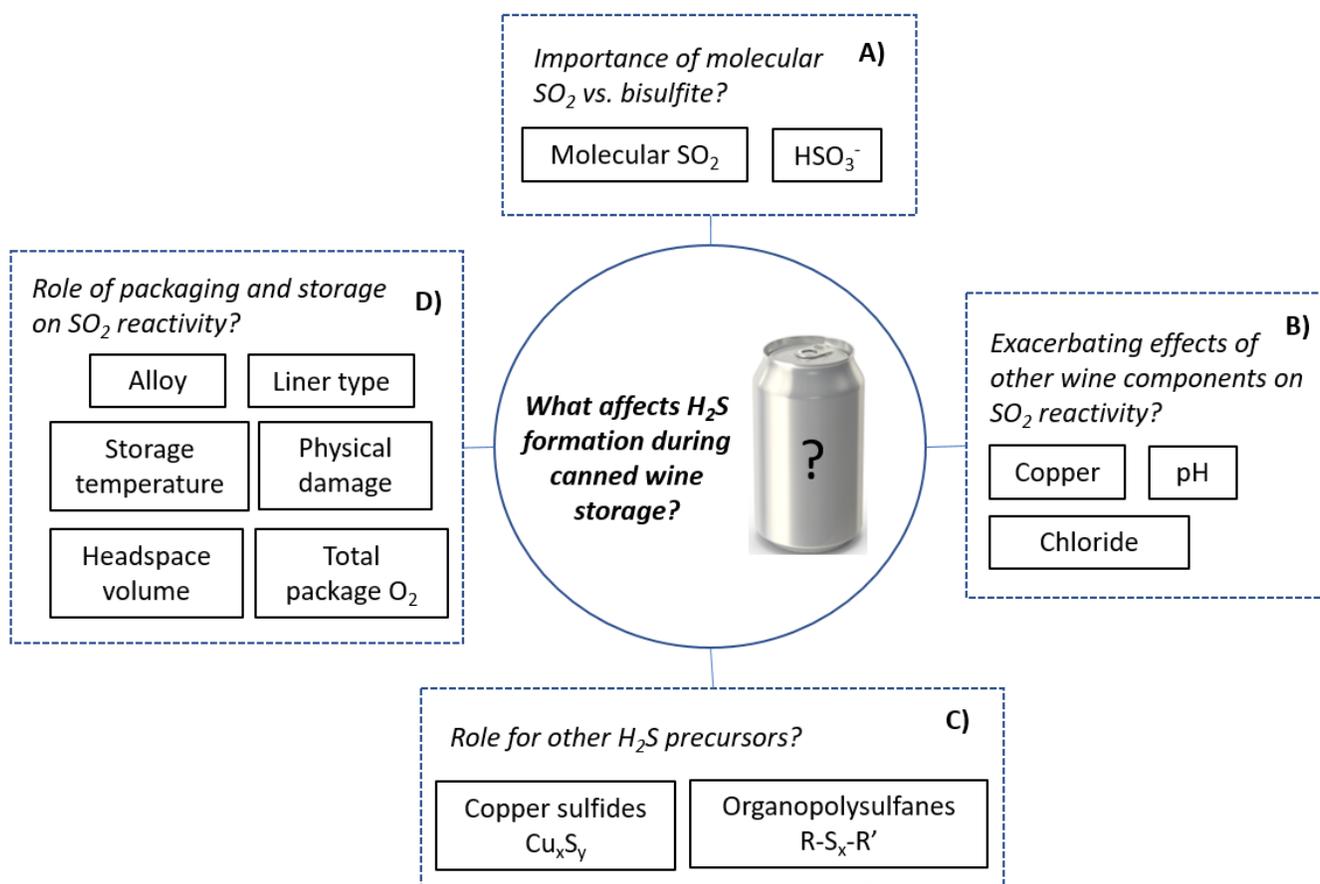


Figure 4. Formation of H₂S in canned wine – questions to be investigated.

Anecdotally, winemakers report less incidence of H₂S with BPA epoxy based liners, although these liners have been declining in usage for reasons previously described (Bomgardner 2019). The first generation of BPA – non-intent (BPA-NI) liners for wine cans was reported to have more problems with H₂S formation. However, more recent generations of liners are reported to have better performance.

The potential role of other wine components.

Wine is acidic, in a range (pH 3-4), which is also typical of other canned beverages (e.g. juice, carbonated soft drinks). For example, many carbonated soft drinks have a pH of <2.5. By itself, pH is not expected to cause storage problems due to the protective action of the can liner. However, lower pH will favor higher proportions of molecular SO₂, which may be the more active form of sulfur dioxide.

Additionally, protons (H⁺) will directly participate in the reaction of SO₂ with Al. Other trace components, such as chloride (Cl⁻) and copper (mostly in the form of Cu[I] in wine) are known to participate in or accelerate aluminum corrosion, although existing data is for non-wine systems (Vargel 2004). Thus, in addition to recommendations for SO₂, can manufacturers typically provide recommendations for Cu, Cl, and pH, along with several other compo-

sitional parameters (Stokes and Barics 2014).

Two caveats should be considered with these recommendations. First, the rationale behind restricting all listed components is not always evident based on existing literature. Second, these recommendations consider each component separately, even though they likely interact synergistically in accelerating corrosion reactions between the can and the beverage components.

Questions, questions, questions.

The recent growth in canned wines is exciting for both wine consumers and producers. Beyond their obvious advantages in convenience, light weight, strength, and visual appeal, the inherent recyclability of aluminum cans makes them an attractive alternative to both glass and plastic (or multilaminate) packaging.

For producers concerned about the potential for H₂S formation during canned wine storage, there is good circumstantial evidence that SO₂ is a key source, although it is unclear if molecular SO₂ or bisulfite is the more important species. For wines where microbial spoilage is of low concern, i.e. sterile filtered wines without residual sugar, the primary role of SO₂ is as free SO₂ to prevent oxidative spoilage.

Because cans allow little oxygen to enter a wine during storage, it may be appropriate to use lower free SO₂ in cans (15-20 mg/L) than what is typically recommended for table wines at bottling, as long as best practices are used to ensure low total package oxygen. Also, most red wines have low free and molecular SO₂ due to binding by anthocyanins (Coelho et al. 2015)⁴ – this factor may explain why winemakers rarely report H₂S formation during storage of red wines in cans. Beyond SO₂ concentrations, there are many other questions surrounding H₂S formation to be answered (Figure 4).

In the longer term, there is a need for validated tools for predicting H₂S formation during canned wine storage. Ideally, this will be more sophisticated than existing tools provided by can manufacturers, which are based on limits for individual wine components (which ignores potential synergies) or corrosion potentials (which assumes that the corrosivity of a wine will be correlated with its ability to form H₂S).

Instead, there is a need to develop and validate accelerated tests, whether they are based on wine composition or on short-term, high temperature studies. This should allow winemakers to make statements along the lines of “Based on accelerated testing, this wine in this can liner has a 0.1% chance of forming detectable levels of H₂S after 6 months storage at room temperature, or after 2 months at 35 °C”. Developing such evidence-based tools to predict quality and shelf-life of canned wines will help producers manage changes in product or package composition, and expand opportunities for canned wine producers.

If you are interested in working with our team at Cornell as we address these questions, please reach out to Gavin Sacks (gls9@cornell.edu) and Julie Goddard (goddard@cornell.edu).

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- ⁴ The actual free and molecular SO₂ of a red wine is typically only 30% of what is measured by aeration-oxidation and related techniques which disrupt anthocyanin-bisulfite complexes during measurement
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Gavin Sacks is Professor and Associate Chair of Food Science, and his research and teaching programs focus on the flavor chemistry of foods and beverages, especially wines and grapes.



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