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Research Article

Hydrogen Sulfide Formation in Canned Wines under Long-Term and Accelerated Conditions

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Key words: accelerated aging, aluminum can packaging, BPA, canned wine, hydrogen sulfide, sulfur like off-aroma,

Background and goals. Wines in aluminum beverage cans (“canned wines”) are a rapidly growing packaging segment due to several factors, including convenience and sustainability advantages. However, canned wines have higher concentrations of hydrogen sulfide (H_2S; “rotten egg”) than wines in glass packaging. It was hypothesized that wine composition and liner selection affect H_2S formation in canned wines.

Methods and key findings. Commercial wines (n=10) were stored in either glass or aluminum beverage cans with one of three liners for up to 32 weeks. Wines stored in glass showed

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negligible H_2S production after 32 weeks. Wines stored in acrylic lined cans produced up to 1307 µg/L H_2S (median = 162 µg/L) within 8 weeks. Wines stored in BPA epoxy cans produced less H_2S (maximum = 51.8 µg/L median = 11.8 µg/L after 32 weeks), with comparable performance observed for BPA non-intent (BPA-NI) epoxy liners. H_2S formation was well-correlated with visible damage to the interior liners, but poorly correlated with dissolved aluminum. H_2S from accelerated aging of wines with lined aluminum coupons (50 ºC, up to 14 d, anoxic conditions) correlated with H_2S produced during long-term aging, but not with H_2S produced by unlined aluminum coupons. Molecular SO_2 was best correlated with increased H_2S production in epoxy lined cans during long-term aging of commercial wines, and similar results were observed under accelerated conditions with coupons in a model-wine factorial experiment. **Conclusions and significance.** Maintaining low molecular SO_2 (less than ~0.4 mg/L) and using epoxy liners (BPA or BPA-NI) appear critical for ensuring low H_2S during long-term can storage up to 8 months. The accelerated aging approach described in this work may be applicable to other corrosive beverages.

Introduction

The global value of wines packaged in aluminum beverage cans ("canned wines") is projected to increase considerably between 2021 (235.7M US Dollars) and 2028 (570M USD) (Romano 2022). Several explanations have been proposed for increased consumer interest in canned wines, including their lighter weight, reduced breakability, aesthetics, and appropriateness for single-serve usage (Williams et al. 2019). Additionally, aluminum is recycled at a higher rate than either glass or polyethylene terephthalate (PET), which provides further appeal to consumers concerned about packaging waste (US EPA 2018).

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Compared to many other types of wine packaging (e.g. glass with screwcap, synthetic, or natural cork closures; Bag-in-Box) (Revi et al. 2014, Crouvisier-Urion et al. 2018), the effects of beverage cans on wine chemistry and sensory properties have not been well described in the peer-reviewed literature, although some information has been reported through extension bulletins, trade journals, conference proceedings and patents (Thompson-Witrick et al. 2021, Scrimgeour et al. 2019, Allison et al 2020, Coetzee 2021, Stokes et al. 2012). A major concern for winemakers with any packaging is oxygen exposure and subsequent wine oxidation (Revi et al. 2014, Crouvisier-Urion et al. 2018). However, the excellent barrier properties of a can double seam allow for trivial amounts of oxygen exposure to a beverage assuming initial total package oxygen is controlled (Torres et al. 2015). One report determined that a typical 355 mL beer can allows in 0.04 mL of air during a 12 week of storage period (Wisk et al 1987). Assuming an O_2 content of air of 21%, this amount of air equates to an ingress rate of 0.1 mg O_2/L per year. This ingress rate is lower than rates reported for glass bottles under a range of closures (Dimkou et al. 2011) and would result in a negligible decrease of total SO_2 (<0.5 mg/L per year) based on the expected 2:1 molar stoichiometry of total SO_2 loss vs. O_2 consumption in wine (Danilewicz et al. 2018).

While oxidation in canned wines is less of a concern, the appearance of so-called "reduced" or "sulfur-like" off-aromas is of great concern to canned wine producers. A recent survey of commercial wines (Allison et al. 2022) reported that concentrations of H_2S ("rotten egg" aroma) in canned wines averaged >10-fold higher than concentrations in glass packaged wines (13.5 vs. 1.1 µg/L) with all canned wines containing H_2S above sensory threshold (~1 µg/L, Siebert et al. 2010). Multiple non-volatile precursors capable of releasing H_2S under anoxic

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storage conditions have been identified, including organopolysulfanes and copper-sulfhydryl complexes (Kreitman et al. 2019). H_2S in wine is readily lost through oxidation reactions, and thus higher concentrations of H_2S in canned wines could simply be a consequence of better oxygen inclusion as has been observed with low-oxygen ingress screwcaps used on glass bottles (Lopes et al. 2009). However, there is evidence that elevated H_2S in canned wines is not solely due to release of H_2S from these known precursors, but rather arises from specific chemical reactions between the can and the wine are involved. Indeed, a 1937 study by Mrak et al. demonstrated that wine stored in the presence of aluminum alloy shavings rapidly forms H_2S-like off aromas (Mrak et al. 1937). This work from almost 100 years ago was concerned with the use of different metals in the winery (e.g. for tank production), as aluminum beverage cans were not in use at the time. A trade journal article with a similar focus cautioned winemakers to avoid use of aluminum materials in wineries, as contact of the metal with either wine or model wine solutions containing SO_2 produced H_2S (Rankine 1983). The formation of H_2S was hypothesized to proceed through the following reaction:

$$2\ Al^0_{(s)} + SO_{2\,(aq)} + 6\ H^+_{(aq)} \rightarrow 2\ Al^{3+}_{(aq)} + H_2S_{(g)} + 2\ H_2O \quad \text{(Eq 1)}$$

This reaction is thermodynamically plausible and is cited in a patent (Stokes 2012) and technical bulletin (Coetzee 2021), although confirmation of its occurrence is missing from the peer-reviewed literature is lacking. These publications stated that limiting SO_2 in canned wines was necessary to prevent H_2S formation by the reaction proposed in Eq. 1. For example, one technical bulletin recommends limiting free $SO_2 < 20$ mg/L, total $SO_2 < 75$ mg/L, molecular $SO_2 < 0.2$ mg/L for canned wines (Coetzee 2021). Recommended limits for other components like

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pH, alcohol, dissolved copper, and dissolved chloride are also provided in that bulletin, although no references or peer reviewed literature are provided for justification.

Although the reaction of SO_2 with aluminum is not well studied, considerable research exists on corrosion of aluminum in aqueous, acidic conditions typical of most beverages. Aluminum metal (Al^0) rapidly forms a passive layer of aluminum oxide (Al_2O_3) in the presence of air or water (Vargel 2004). In low pH, low oxygen systems (typical for most beverages), corrosion of unlined aluminum cans begins with dissolution and thinning of the passive layer, followed by coupled anodic (formation of Al^{3+}) and cathodic (production of H_2 gas) reactions.

$$2\ Al^0_{(s)} + 6\ H^+_{(aq)} \rightarrow 2\ Al^{3+}_{(aq)} + 3\ H_{2\ (g)} \quad \text{(Eq 2)}$$

These reactions are accelerated at lower pH, and in the presence of components like copper (both ions in solution as well as impurities in aluminum alloys), which will integrate into Al to facilitate cathodic reactions; and chloride, which forms $AlCl_4^-$ and facilitates the anodic reaction (Vargel 2004). These corrosion reactions can lead to leaking and loss of the hermetic seal in unlined beverage cans, and the resulting increase in dissolved Al could affect flavor, cause hazes, and be of concerns to human health (Klotz et al. 2017, Tariba 2011).

To slow corrosion reactions like that shown in Equation 2, beverage can manufacturers coat the can interior with a thin (1-10 µm) non-porous liner material, also referred to as an "enamel", "lacquer" or "coating" (Crouchiere 2020). Historically, most beverage can liners consisted of bisphenol A (BPA) epoxy resins, but recent regulations concerning BPA usage have resulted in producers evaluating other options for liner materials. These "BPA – non-intent" (BPA-NI) alternatives include older acrylic and polyester liner technologies as well as newer epoxies that utilize monomers other than BPA, e.g. bisphenol F (Soto 2017).

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Peer-reviewed literature on effects of SO_2 or other components on corrosion, H_2S formation, or other unwanted reactions during beverage can storage is non-existent for wine and limited for other beverages. One group observed modest variation in the increase in dissolved Al (0.3-1.2 mg/L) among seven carbonated sodas over 12 months storage, which the authors attempted to explain as resulting from the higher citric acid and lower pH of certain samples (Seruga et al. 1994). Another study observed comparable dissolved Al for seven of nine drinks evaluated, although two of the drinks showed much higher dissolved Al concentrations (up to 74 mg/L after 29 months). The authors again credited the greater dissolved Al concentration of one beverage (juice) to its higher citric acid content. One challenge with interpretating these and related studies is that commercial canned products are typically used, and thus the researchers cannot know if the cans used identical liners or had been stored in a similar manner before purchase. One exception is a recent report which evaluated canning of ethanol-based hand sanitizers using two liner types (epoxy and BPA-NI). The authors concluded that high ethanol (75-85% v/v) causes rapid liner degradation and corrosion as compared to other sanitizer components (0.125 % H_2O_2 and 1.45 % glycerol). Another report (Soares et al. 2019) used a combination of dissolved Al and electrochemical approaches to evaluate the effects of varying concentrations on Cu and Cl^- in model beverage systems on corrosion and concluded that liner variability outweighed composition in importance. However, the validity of extending these reports to commercial wines is uncertain.

The poor documentation of the effect of wine liner type and wine composition on can corrosion and H_2S formation in the peer reviewed literature creates a challenge for meeting producer and consumer interest in expanding production of beverages packaged in aluminum

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cans. In this work, we report a study on the formation of H_2S in canned wines as a function of liner type and wine composition in comparison to glass after up to 8 months storage. Additionally, we develop and describe a (<14 d) convenient accelerated aging assay using lined Al coupons and validate the accelerated study against long-term storage studies for evaluating wine components likely responsible for H_2S formation. While this work is immediately useful for winemakers to utilize as a resource for quality winemaking in cans, there is also potential for this work to be applicable to any other beverage stored in aluminum beverage cans.

Materials and Methods

Materials and Chemical Reagents. Liquid nitrogen (LN2) and nitrogen gas (UHP) were obtained from Airgas (Elmira, NY). A 500 mL LN2 sprayer was obtained from US Solid (Cleveland, OH). Headspace vials (30 x 60 mm, 27 mL), 20 mm butyl rubber septa, and 20 mm tear away crimp seals, and 20 mm hand crimper were all obtained from Supelco (Bellefonte, PA), (product codes 27298, Z166065, 27016, and 33280-U, respectively). A 5-25 mL bottle-top dispenser was obtained from VWR (Radnor, PA) (82017-768). A 1000 mL glass bottle, coated, clear w/ septa port was obtained from Ankom Technology (Macedon, NY). Surebonder electric glue skillet and Surebonder B-2001 hot glue pellets were obtained from Amazon (Seattle, WA). Double-side-coated sheets of coated 3004 aluminum and 355 mL aluminum beverage can bodies were provided by an industry cooperator. Coatings were identical to commercially available coating options, and included BPA epoxy, Gen II BPA-NI epoxy; and Acrylic (3.22 micron coating thickness). Can ends (5000 series alloy, BPA Epoxy 202LOE B64 style, American Canning, Austin, TX) were obtained from the same industry collaborator. The Oktober MK16 can seamer were obtained from Oktober Design (Grand Rapids, MI). A 22.7 L water cooler was

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obtained from a local Walmart (Ithaca, NY). An aeration-oxidation apparatus was obtained from GW Kent (Ypsilanti, MI). Gastec detection tubes (Gastec International, Sand Diego, CA) used for analyses of H_2S (4LT and 4LL) and SO_2 (5L) were purchased from Airgas (Radnor, PA) and Grainger (Lake Forrest, IL). Ethanol (EtOH), 70% v/v, was purchased from Koptec (King of Prussia, PA). L-(+)-tartaric acid (99%) was purchased from Acros Organics (Morris Plains, NJ). Sodium hydroxide pellets were obtained from Fischer Scientific (Waltham, MA). Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 99%) was purchased from Beantown Chemical (Hudson, NH). Acetaldehyde (CH_3CHO, 99%) was purchased from Alfa Aesar (Ward Hill, MA). Potassium Metabisulfite ($K_2S_2O_5$, 99%) was purchased from Fisher Scientific (Waltham, MA). Perchloric (70%) and nitric acid (70%) were obtained from GFS (Columbus, OH) and Fisher Scientific (Waltham, MA) respectively, and redistilled into a Teflon vessel under infrared light.

Commercial Wines and Initial Chemical Analysis. Glass-packaged wines (n = 10; six white, two rosé, and two red) were purchased from a local retailer in Ithaca, NY. Wines were selected to be representative of a broad range of wine regions, varieties, and styles. Wines were coded, and their initial chemistry is reported in Table 1. Dissolved copper and aluminum were analyzed at a local facility (USDA-ARS Holley Center; Ithaca, NY) using a Thermo iCAP 6500 series Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Ithaca, NY) by a protocol described in a later section. Chloride was measured with a SympHony Combination Chloride Electrode (VWR International; Radnor, PA) using the manufacturer's protocol. All other wine analyses were performed by the Cornell Craft Beverage Analytical Laboratory (Geneva, NY) using standard protocols; alcohol by volume was determined by OenoFoss (Foss; Hillerod, Denmark); free and total SO_2 were determined by flow injection (Foss FIAstar 5000

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Analyzer; Hillrod, Denmark), titratable acidity (TA) was measured by autotitration (Metrohm 862 Compact Titrator; Herisau, Switzerland); pH was measured on a Fisher Scientific Accumet Excel XL25 dual-channel pH/ion meter (Pittsburgh, PA), and fructose + glucose was measured enzymatically (Randox RX Monaco; Crumlin, UK). Molecular SO_2 was manually calculated in the following equation using pKa values adjusted for alcohol as described by (Sacks et al. 2015):

$$Molecular\ SO_2 = \frac{Free\ SO_2}{1+10^{pH-pKa}}$$

Real-time Storage Stability Study. For each wine, 15 L (twenty 750 mL bottles or ten 1.5 L bottles) were loaded into a 20 L plastic water cooler, previously sanitized by a 70% ethanol rinse. The cooler and wine were purged with nitrogen gas until oxygen was < 0.1 mg/L (Fibox 3 LCD trace O_2 meter w/ DP-PSt6 oxygen dipping probe; Presens, Regensburg, Germany). A steady flow of nitrogen gas was introduced to backfill the cooler during can filling to prevent oxygen pickup.

Can bodies (355 mL; 3004 alloy) coated with one of three liner types; BPA epoxy, Gen II BPA-NI epoxy; and Acrylic, and lids (5000 series alloy, BPA Epoxy 202LOE B64 style, American Canning, Austin, TX) were rinsed with 70% ethanol before use. Just prior to filling, a few mL of LN2 was added to the can body to expel oxygen and retain can pressure. Once the LN2 had nearly evaporated, wine was dispensed from the cooler to fill the can body. Fill level was monitored by weighing cans during filling. Following filling, two drops of LN2 were added to remove headspace oxygen, and the can was immediately topped with a lid and seamed on a manual double seamer (MK16 seamer; Oktober Design; Grand Rapids, MI). Seam quality was validated using an industry standard tear down protocol (first operation seam thickness, 0.074 in – 0.078 in; second operation seam thickness, 0.042 in – 0.046 in; cover hook length, 0.053 in –

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0.065 in; body hook length, 0.055 in – 0.075 in). Total package oxygen (TPO; sum of oxygen in liquid and headspace, normalized against volume) was evaluated by allowing the newly seamed cans to rest for 1 hr, followed by gently agitating the can to equilibrate headspace and liquid, then opening the can and measuring the oxygen concentration of the liquid by dipping probe. Using this protocol, TPO was determined to be <1.5 mg O_2/L for tested cans.

Following seaming, cans were stored at 20 ° C in an upright position, away from sun and light until analysis at one of four time points (1-, 2-, 4-, or 8-months storage; 3 storage replicates for each wine and each time point). The longest time point (8-months) was selected to correspond to the minimum shelf life desired by regional canned wine producers (personal communications). Due to shortage of BPA-NI epoxy cans, W6 could not be packaged in the BPA-NI lined can. Unopened control wines in original glass packaging were stored under the same conditions and analyzed at the end of the eight-month period except for wine W6, for which a measurement at five months was used due to lack of supply at the later time period. The unopened control wines differed in their closures (screwcap vs. natural corks), and the likelihood of this difference affecting H_2S accumulation is considered in the Results and Discussion.

Accelerated Storage Stability Study. For each accelerated aging sample, aluminum coupons were placed in a clear glass crimp-top vial (27 mL headspace vial, Item 27298, Supelco, Bellefonte, PA) followed by purging with 2-3 drops of LN2 and finally dispensing of 25 mL of wine. Vials were then lightly capped with 20 mm butyl rubber septa to allow excess LN2 to dissipate and to prevent cracking of the vials due to excess pressure (typically, about 10-15 s). Vials were sealed with a 20 mm aluminum metal crimp cap and stored at elevated temperature

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prior to H_2S measurement. Further information on lined coupon preparation, dispensing wine, and temperature storage conditions are provided below.

A two-necked glass bottle (1000 mL, coated, clear w/ septa port, Ankom Technology, Macedon, NY) was used for deoxygenating and dispensing wine samples. The side-arm of the bottle was fitted with a screwcap septum closure. 20 °C wine (typically, 750 mL) was loaded into a two-necked glass bottle and deoxygenated for 3 min (O_2 < 1.5 mg/L) with N_2 gas; the time required for deoxygenation was determined in initial work using non-invasive PreSens sensor spots (SP-PSt6, Presens, Regensburg, Germany). Following deoxygenation, a small amount of LN2 was added and the bottle capped with an adjustable 5-25 mL bottle top dispenser. N_2 gas was trickled via a needle through the side arm port septum to maintain the inert headspace. The presence of a pressure relief valve at the base of the bottle-top dispenser prevented over-pressuring of the dispenser. Prior to loading sample vials, 75 mL of wine was discarded to purge the dispenser lines.

In initial studies to determine appropriate septum materials, replicate 27 mL vials affixed with PreSens sensor spots (SP-PSt6-YAU, PreSens, Regensburg, Germany) were filled with deoxygenated water using the protocol above, and closed with one of four different septum materials (butyl rubber, silicone, PTFE/silicone, isoprene) and stored for up to 7 d at 40 °C. Dissolved oxygen was measured using a PtS6 optical SMA attached to a Fibox 3 LCD Trace dissolved oxygen meter (Presens, Regensburg, Germany). Based on this work, butyl rubber septa were determined to provide the best performance in limiting oxygen ingress. Total package oxygen for samples sealed with butyl rubber septa at 50 °C was then determined using a similar

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253 experiment, except that dissolved oxygen was measured at regular intervals for up to 14 d (n =
254 10 replicates).

255 Coated aluminum coupons (1 cm × 4.5 cm) were cut by shears from sheets of coated
256 3000-series aluminum alloy (18 µm total thickness; coating thickness = 3.2 µm) provided by an
257 industry collaborator. The coatings were the same composition of the beverage cans (BPA
258 epoxy, BPA-NI epoxy, Acrylic). Following cutting, the edges of each coupon consisted of
259 uncoated aluminum. These bare edges were sealed with an ethyl vinyl acetate (EVA) hot melt
260 glue (B-2001 Pellets, Surebonder, Seattle, WA) and allowed to air dry (~ 30 s). Ethyl vinyl
261 acetate was chosen due to ease of application and non-reactivity with H_2S, as discussed in the
262 results.

263 To evaluate the ability of hot-melt glue to prevent formation of H_2S by wine-aluminum
264 contact, unlined aluminum coupons were either coated entirely in hot-melt glue or left uncoated
265 as controls. To confirm that the hot melt glue did not react with evolved H_2S, unlined aluminum
266 coupons were prepared with and without edges coated with hot melt glue. Coupons were then
267 incubated in a white wine with undetectable initial H_2S for 3 d at 50 °C under the accelerated
268 aging conditions described above, after which H_2S was measured using the GDT assay.

269

270 **Characterization of stored wines – H_2S, visual inspection, and dissolved aluminum**.
271 H_2S was measured using a modified aeration-oxidation (A-O) apparatus with quantitation by gas
272 detection tubes (GDT) (Allison et al, 2022). Briefly, an H_2S GDT was attached in series between
273 the receiver flask of the A-O apparatus and the vacuum source. During an analysis, the sample
274 was aspirated, resulting in a stain forming on the GDT via reaction of H_2S with a metal salt in the

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tube. The length of stain on the GDT is proportional to the original H_2S concentration. To prevent interferences from SO_2, an SO_2 GDT and a flask containing aqueous acetaldehyde solution were placed in series prior to the H_2S GDT. The calibration was performed using five standards over the range of 0-86 µg/L for 4LT tubes, and 0-380 µg/L for 4LL tubes with 60 mL of standard solution (Allison et al, 2022). For wines, to prevent saturation of the GDT from high H_2S samples, analyses were initially performed with 10 mL of sample, which could subsequently be increased to up to 60 mL, depending on H_2S concentration. The methodological detection limit was ~1 µg/L.

For visual inspection of can corrosion, can tops and bottoms were cut via band saw (Gryphon C-40 Band Saw, Gryphon Corporation, Sylmar, CA), then cut lengthwise with scissors. Can samples were scored on a 0-5 scale by a single individual (A. Montgomery) to ensure consistency. Cans with no visible corrosion were scored "0" and those with the maximum observed level of corrosion were scored "5". The entire can interior was considered in the evaluation.

Dissolved aluminum was measured via ICP-OES. Wine (2 mL) was pipetted into glass vials and allowed to evaporate to dryness at 60 °C for 3 d. Dried samples were digested by addition of 60:40 HNO_3:$HClO_4$ (3 mL) in a Pyrex glass tube, storing overnight at room temperature; then heating the samples at 70-120 °C for two hours, followed by 145 °C until brown color is depleted. If samples had any residual brown color, additional concentrated nitric acid (up to 2 mL) was added. Then, the temperature of the heating block raised to 190 °C for 10 min, and the samples allowed to cool to room temperature. Cooled samples in the tubes were diluted to 10 mL, vortexed, and transferred to ICP autosampler tubes. Appropriate standards

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were prepared in 2% $HClO_4$. Aluminum was measured at 396.152 nm in axial view mode by ICP-OES (Thermo iCAP 6500 series, Thermo Scientific, Waltham, MA).

Validation of Accelerated Storage Stability Study. Different bottles of the same commercial wines in the same lot used in long-term can studies underwent accelerated aging with one of three lined coupons using the protocol described above. Wine samples were then incubated in darkness for either 3 d or 14 d at 50 °C. All Wine × Liner × Storage Time treatments were performed in replicate (n = 6 (BPA Epoxy), n = 3 (BPA-NI Epoxy)). At the end of storage, H_2S was measured in all samples by the GDT assay. Accelerated aging was also evaluated using unlined (bare) Al 3000-series alloy coupons (1 cm x 4.5 cm) for a subset of wine samples.

Effects of pH, Free SO_2, ethanol, and molecular SO_2 on H_2S formation under accelerated conditions. Starting from a base wine, wines of varying compositions were prepared based on a partial-factorial model to systematically investigate the role of pH, free SO_2, molecular SO_2, and ethanol on H_2S production. Values for pH, free SO_2 and ethanol were selected to bracket the extremes found in wines (Waterhouse et al. 2016). Three separate partial factorial experiments were conducted, but all samples contained the same base: W3, which produced the lowest amount of H_2S among the white wines studied. To achieve different ethanol levels, 70% ethanol or DI water were added to the base wine such that that the extent of dilution was consistent across treatments. The first set of experiments used constant ethanol (13% v/v) and free SO_2 (50 mg/L), with pH at 6 different levels (2.75, 3, 3.25, 3.5, 3.75, and 4). The second experiment contained two levels of ABV (8 and 18%), three levels of pH (2.9, 3.3, 3.8), and free SO_2 varied from 19 mg/L to 368 mg/L to create two levels of molecular SO_2. The final

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experiment used constant ethanol (8% v/v), three levels of pH (2.8, 3.2, and 3.6) and three levels of free SO_2 (20, 50, and 80 mg/L). In all experiments molecular SO_2 at 20 °C was calculated from free SO_2 and pH using the Henderson-Hasselbalch equation with temperature and alcohol corrected pK_a values of SO_2 (Coelho et al. 2015).

Statistical Analysis and Software. Statistical analysis was done via JMP Pro 16 (SAS Institute Inc., Cary, NC). ANOVA ($\alpha = 0.05$) was used to evaluate the effects of storage time, liner, and wine on H_2S production. Multiple linear regressions were used to evaluate correlations between wine composition and H_2S production, dissolved Al, and liner degradation. Linear regressions ($p<0.05$) were used to evaluate the agreement between room temperature and accelerated storage conditions.

Results

H_2S in canned wines vs. glass – effects of storage time and liner type. Ten glass packaged commercial wines were repackaged in cans with one of three liners (BPA epoxy, BPA-NI epoxy, and acrylic), and H_2S measured after 1-, 2-, 4-, and 8-months storage, with H_2S produced after 8 months in wines stored in their original glass packaging as control (Figure 1). For BPA epoxy lined cans, H_2S concentrations increased in all canned white and rosé wines in a time-dependent manner (linear regression, $p <0.05$) to concentrations above the H_2S sensory threshold in wine (~ 1 µg/L). A significant increase in H_2S was observed for two of the white wines (W2, W6) after only two months, and for all white and rosé wines by either 4 or 8 months for both BPA and BPA-NI liners. For the two rosé wines and four of the six white wines, the highest H_2S concentration was observed at the final 8-month time point. However, the two highest H_2S concentrations (43 µg/L in W2 and 53 µg/L in W6) were observed after 4 months

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can storage. Negligible H_2S production was observed in the two red wines. Relatively high can-to-can variation in H_2S formation was observed – considering only BPA-epoxy lined cans, average RSD was 69% and 55% for cans stored for 4 and 8 months respectively. High can-to-can variation has been observed previously and has been credited to variation in liner thickness and heterogeneity in the aluminum composition.

The same ten commercial wines were also stored in their original glass packaging and analyzed after 8 months of canning (Soares et al. 2019). Due to limited supplies, glass packaged W6 was not available at 8 months; however, H_2S had been measured in this wine after 5 months storage as part of a quality control check, and this value is included instead. After long-term storage, H_2S was undetectable (< 1 µg/L) in most of the glass-packaged wines, with a maximum value of 5.2 µg/L in the R2 wine. No significant difference in H_2S accumulation was observed as a function of closure (screwcap vs. natural cork) in the unopened controls, indicating that this factor was unimportant in H_2S formation in the current experiment. H_2S concentrations after 8 months storage in glass were significantly lower than the range observed in BPA-epoxy cans after 8 months (paired t-test, $p<0.05$), in agreement with a recent survey of commercial wines in a separate report (Allison et al. 2022). Full results from BPA-NI and acrylic lined cans are reported in Supplementary Figure 1. H_2S formation following 8 months storage in BPA-NI epoxy and BPA epoxy lined cans is well correlated ($r^2 = 0.69$; Figure 2). Similar correlations can be observed for BPA-NI epoxy, however acrylic lined coupons showed a poor correlation with long term storage. (Supplementary Figure 2).

Wines in acrylic lined cans rapidly formed suprathreshold concentrations of H_2S. After only one month of storage, median H_2S concentrations in acrylic cans (367 µg/L) were greater

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than the highest value (35 µg/L) reported in a survey of wines with "reductive" flaws (Siebert et al. 2010). The maximum H_2S production in acrylic-lined cans (1307 µg/L) was over 20-fold higher than in either BPA or BPA-NI epoxy lined cans, and formation across all wines was poorly correlated with production of H_2S for the same wines in BPA epoxy cans (r^2=0.008; Figure 2).

H_2S formation during long-term storage correlates with visible damage to the liner, but not dissolved aluminum.

Visible damage to the can liners was scored on a 0-5 scale (0 = no damage, 1 = slight damage to headspace region of body, 2 = slight damage to headspace and submerged regions of body, 3 = obvious damage to headspace, 4 = obvious damage to headspace and submerged regions of body, 5 = delamination of liner) and data are reported in Supplementary Figure 3. Examples of an undamaged (score = 0; undamaged BPA epoxy) liner and badly damaged liner (score = 5; acrylic undergoing delamination) are shown in Figure 3. Damage to the liner took the form of small blisters (diameter up to 2 mm), with no evidence of any material deposited on the surface. Blister appearance was similar to that which was reported for blisters formed in beverage cans following exposure to high alcohol hand sanitizers (Thomson et al. 2020). As with H_2S production, liner damage was not detected for most wines until after 4 months. The extent of damage to the BPA epoxy and BPA-NI epoxy can liners was well correlated with H_2S formation at 8-months storage (Spearman's test, $\rho < 0.05$; Figure 4.)

Aluminum corrosion under acidic, anoxic conditions results in the oxidation of insoluble Al (0) to soluble Al (III) species and concurrent formation of H_2 gas (Equation 2), and thus measurement of dissolved aluminum is proposed as a proxy for corrosion during beverage can

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storage (Soares et al. 2019, Scrimgeour et al. 2020). To determine if the change in dissolved aluminum (Δ[Al]) and H_2S formation were correlated, [Al] was measured in initial wines and subsequent storage points in the canned wines. Initial concentrations of dissolved aluminum in wines ranged from 0.5 - 2.1 mg/L, in agreement with a recent report (Karas et al. 2020). No significant increase in [Al] was observed until 4 months. Concentrations increased with storage time after 4 months and reached a maximum after 8 months for most wines. The highest Δ[Al]) for the BPA epoxy liner was observed for W2, which was 2.29 mg/L after 8 months, comparable to the increase in [Al] observed in a recent report on canned wines (Scrimgeour et al. 2020). A strong correlation was observed for Δ[Al]) for the BPA epoxy and BPA-NI epoxy liners by 8 months storage time (r2 = 0.928; slope = 1.03; figure not shown). Like H_2S, Δ[Al] was much higher in acrylic-lined cans; Δ[Al] values as high as 4.49 mg/L were observed after 2 months. Because of the poor performance of the acrylic liners, no Al measurements were performed at 4 or 8 months.

Δ[Al]) was only weakly correlated with H_2S formation from 1-8 months storage (R^2=0.189, Figure 5a). After 8 months storage, regression coefficients for Δ[Al]) and H_2S were r^2 = 0.45 for epoxy coated cans (designated by squares in figure 5a). As a caveat, dissolved Al or H_2S could be lost from certain wines following their formation, e.g., Al (III) may form insoluble complexes with proteins (Bengough et al. 1954), and thus these measurements may underestimate the extent of H_2S formation and Al oxidation during canned wine storage.

H_2S and Δ[Al]) during long-term storage – correlation with chemical composition. The composition of the ten wines under study was measured prior to canning (Table 1). Measurements included both common wine chemistry metrics (pH, TA, alcohol, residual sugar,

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free SO_2, total SO_2, molecular SO_2), along with components implicated in accelerating beverage can corrosion (copper, chloride) (Coetzee 2021). The observed ranges for most compounds in this study were generally representative of ranges reported in other surveys of commercial wines. For example, chloride concentrations were well distributed from 32 to 442 mg/L, which mostly covers the range of values reported in a survey of table wines (Coli et al. 2015). The only chemical parameter that was not effectively represented was copper. All wines in this study contained <0.1 mg/L Cu except R1 (0.39 mg/L). These values were comparable to those reported in large survey of commercial Australian wines (Martin et al. 2012), but the uneven distribution of Cu concentrations was not well suited for correlation analyses.

Linear regression analyses of [Component] vs. [Avg of H_2S at 4 mo. and 8 mo.] were performed for each component. The average H_2S at 4 and 8 months was used for regression analyses to account for variation in the timing of "peak" H_2S. The chemical parameters best correlated with H_2S formation were free SO_2, molecular SO_2, and pH, all with correlation coefficients of $|r| > 0.8$ (Figure 6a). A more modest correlation with H_2S production was observed for TA ($r = 0.6$), and lower correlations of $|r| < 0.4$ were observed for Cu, Cl^-, alcohol, residual sugars (glucose + fructose), and total SO_2. Multiple linear regressions were also performed for [Component] vs. Δ[Al] data after 4 and 8 months. No significant correlation was observed at the 4-month point for any component, but two components (pH, $r = -0.59$ total SO_2, $r = 0.61$) was correlated with Δ[Al] after 8 months.

Development of accelerated aging test for prediction of H_2S formation during long-term storage. An accelerated test based on storage of lined aluminum coupons (1 cm × 4.5 cm × 18 μm) incubated in crimped vials filled with 25 mL of a test wine was developed and validated.

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This approach was taken instead of performing accelerated aging on beverage cans to save on cost of materials and minimizing space for storage of cans. It also allows for faster throughput compared to canning beverages by hand, and limits concerns surrounding the quality of the can seam at elevated temperatures.

Preliminary investigations by our lab into accelerated aging yielded poor reproducibility for H_2S values, even with H_2S spiking experiments and omission of the coupon (data not shown). These poor results were determined to arise from variable and high levels of oxygen, either during packaging or during storage, presumably leading to oxidative losses of H_2S through one of several pathways (Kreitman et al. 2019). The challenge of maintaining low oxygen conditions is made more acute due to the small volumes of wine being handled (25 mL). Other researchers have described the use of anoxic gloveboxes to maintain low oxygen during preparation of wine samples (Franco-Luesma et al. 2016) for storage. In this work, O_2 pickup during vial preparation was minimized by purging and backflushing a dispensing flask with N_2 gas while filling, resulting in undetectable O_2 in the wine even with rapid filling of vials. Headspace oxygen was limited by adding a small amount of LN2 just prior to crimp capping of the vials. With this approach, total package oxygen (as determined by non-invasive sensor spots) could be limited to 0.075 mg O_2, or the equivalent of 3 ± 0.5 mg/L for the sample. Although this value is higher than a typical target for a commercial canning operation, the good reproducibility allowed for acceptable precision for subsequent H_2S measurements following accelerated aging.

Silicone septa and PTFE/silicone septa allowed high levels of oxygen ingress during storage at elevated temperature (5.2 ± 0.4 mg/L and 3.2 ± 0.4 mg/L O_2, respectively after 7 d at 40 °C, respectively (Supplementary Figure 4)), an observation that was unsurprising considering

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the high oxygen permeability of both Teflon and silicone. However, butyl rubber and isoprene septa both allowed negligible amounts of O_2 ingress (<0.02 mg/L pickup after 7 d at 40 °C). Further testing with butyl rubber septa revealed that they allowed negligible oxygen ingress out to 14 d at 50 °C (data not shown), and thus was utilized for future accelerated aging tests.

The use of coupons for corrosion testing is commonplace in industrial settings, as it allows for convenient and reproducible evaluations of metal-solution interactions (ASTM International 2005). For the results in this work, coupons were hand-spin coated by the industry cooperator in the same manner and thickness in which the cans were coated. However, later experiments demonstrated that comparable results could be achieved by clipping coupons from commercial beverage cans with tin shears (data not shown). One challenge with the use of coupons is that edges are unlined, which would allow for bare aluminum to contact the wine, and thus lead to high H_2S formation regardless of coupon coating. Ethyl vinyl acetate was used coat the edges of coupons to protect bare aluminum from interacting from the wine. To confirm that the EVA glue was inert, unlined aluminum coupons were prepared either with bare edges or EVA-coated edges. Both treatments had bare aluminum coupon faces. Following incubation in a white wine under accelerated conditions, no difference in H_2S formation was observed (65 ± 8.7 µg/L for no edge coating vs 67 ± 4.3 µg/L for edge coated), indicated that the EVA glue did not react with evolved H_2S. However, unlined coupons that were fully coated with hot melt glue produced no detectable H_2S, indicating that EVA was an effective barrier to prevent contact between wine and coupon under accelerated conditions.

In preliminary experiments using two test wines, no detectable H_2S signal was observed at 40 °C at 3 d, but H_2S could be detected at 50 and 60 °C for the same period. However, at 60

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473 °C, the hot-melt glue was observed to soften and re-melt, and 50 °C was selected for validation
474 experiments

475

476 **Accelerated aging with lined coupons predicts H_2S following long-term can storage,**
477 **but accelerated aging with bare aluminum coupons does not.**To determine an appropriate
478 storage time for accelerated aging, wine and lined coupons (BPA epoxy, BPA-NI epoxy, acrylic)
479 were incubated at 50 °C using the optimized conditions described above, and H_2S was measured.
480 Control wines with no coupon ("glass storage") and wines stored with bare aluminum coupons
481 were also included. Storage experiments were performed for both 3 and 14 d, except for BPA-NI
482 epoxy coupons where only 3 d storage was evaluated due to limited coupon supply.
483 Representative data for three wines (Red 1, Rosé 1, White 2) are shown in Figure 7. As expected
484 from results with long-term storage, the red wine produced negligible H_2S, and the lined coupons
485 produced H_2S in the order Acrylic > BPA-NI epoxy ~ BPA epoxy. Notably, negligible H_2S was
486 formed in the glass-only control trials performed without coupons.

487 Across all wines, H_2S formed during long-term storage in BPA epoxy cans (average of
488 concentrations after 4- and 8-months storage) was well-correlated with the average of 3 d and 14
489 d accelerated aging with BPA epoxy lined coupons ($R^2 = 0.793$, Figure 8). Acceptable
490 correlation was also observed when using only 3 d or 14 d results ($R^2 > 0.65$, supplementary
491 figure 5). The range of H_2S formed after 14 d of accelerated aging test (0 to 56 µg/L) was
492 comparable to the range observed after 8 months, despite requiring ~17-fold less time. As with
493 long-term aging, H_2S formation with epoxy lined coupons was best correlated with molecular
494 SO_2 ($R^2 = 0.884$, Figure 6a).

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H_2S formation during long-term aging and 3 d accelerated aging conditions was also correlated for BPA-NI epoxy lined cans and coupons (R^2 =0.65, Supplementary Figure 4, top) but poorly correlated for acrylic coupons and cans (R^2 =0.051, Supplementary Figure 4, bottom). Accelerated aging with bare (unlined) aluminum coupons produced higher levels of H_2S formation with up to 955 µg/L formed after 3 d (Figure 8). H_2S production with bare aluminum coupons under accelerated conditions and H_2S production with BPA-epoxy coated cans during long-term storage conditions was uncorrelated ($R^2 < 0.15$, Figure 8).

Validation of impact of molecular SO_2 on H_2S formation. To confirm the importance of molecular SO_2 on H_2S production in the presence of lined aluminum, wine samples (n=24) were prepared with varying levels of ethanol (8, 13, 18%), pH (2.75-4), and Free SO_2 (20-80 mg/L) with W3 used as a base (the white wine which produced the least amount of H_2S following long-term storage). These values resulted in molecular SO_2 ranging from 0.5 – 8.4 mg/L at 20 °C, or 2.06 – 25 mg/L at 50 °C (the temperature of the accelerated aging test). Wine samples were subjected to accelerated aging with BPA epoxy lined coupons, and H_2S measured. Molecular SO_2 was the best predictor of H_2S formation (R^2 = 0.57; Figure 9), and no significant correlations were observed for the other parameters. Notably, these systems did not contain detectable sulfhydryl precursors, e.g. copper-sulfhydryls, since this same wine stored in the same manner without an aluminum coupon produced undetectable H_2S. This indicates that H_2S formation by aluminum requires only the presence of SO_2.

Discussion

Classic research by Mrak, et al reported that wines will develop rotten egg, H_2S-like aromas following contact with aluminum alloys (Mrak et al., 1937), and both the patent literature

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and trade journal articles report that wines packaged in aluminum beverage cans will develop more H_2S during storage (Scrimgeour et al. 2019, Stokes 2015). Higher H_2S concentrations are observed in commercial canned wines than in glass bottled wines (Allison et al. 2022), but a comparative study of H_2S formation of the same wines under canned vs. glass packaged conditions has not been reported in the peer-reviewed literature, despite equation 1 being proposed in 1983 by Rankine.

In this work, multiple commercial wines were stored in either glass or in cans with one of three liners. Wines stored in acrylic lined cans showed highly degraded liners and extreme H_2S production (up to 1300 µg/L, Supplementary Figure 1) after only 2 months and would not be acceptable for commercial use. For BPA and BPA-NI epoxy cans, some white wines developed H_2S above 10 µg/L after 4 months storage at room temperature (Figure 1) and in some cases, in as little as two months. By comparison, most of the glass packaged wines developed no detectable H_2S during the same storage period (Figure 1). With epoxy liners, the wine component that was best correlated with H_2S formation under both long-term and accelerated conditions was molecular SO_2, followed by pH and free SO_2 (Figure 6a). A follow up study using a wine adjusted to varying SO_2 and pH showed that increasing molecular SO_2 yielded a good correlation with H_2S formation, while increasing free SO_2 or pH alone were less predictive (Figure 9). However, because molecular SO_2 will be proportional to [free SO_2] × [H^+], it is unclear if the observed increase in H_2S is due to molecular SO_2, or a synergistic interaction between the free SO_2 and pH.

Based on these results, a likely explanation for the higher H_2S formation observed in many canned wines is the reaction of SO_2 and aluminum to yield H_2S (Equation 1), as

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hypothesized by others (Rankine 1983, Stokes et al. 2012). An alternative potential explanation for the H_2S increase in canned wine is that it is released from precursors (e.g. copper-sulfhydryl nanoparticles) (Kreitman et al. 2019), and preserved under the anoxic conditions of the can. However, several of these wines were packaged under Saranex or Saran-tin screwcaps (wines R2, W1, W2, W4, W5, W6), which should allow low oxygen ingress comparable to cans (Thompson-Witrick et al. 2021). Furthermore, this alternative "precursor-release" hypothesis would not explain why accelerated aging of wines in the absence of coupons result in negligible H_2S formation (Figure 7).

Based on the hypothesis that molecular SO_2 (or free SO_2 × pH) is the cause of H_2S formation during canned wine storage, the data in Figure 6a can be used to estimate a maximum recommended limit of molecular SO_2. As described by Allison, et al, Siebert, et al and references therein (Allison et al. 2022, Siebert et al. 2010). the odor detection threshold of H_2S is ~ 1 µg/L, but the recognition threshold is possibly as high as 30 µg/L. Using an intermediate target of maintaining H_2S below 10 µg/L, the maximum recommended limit for molecular SO_2 is 0.4 mg/L. This recommendation is based on a targeted shelf-life of approximately 6 months and room temperature storage, but this limit would need to be decreased if longer shelf-lives were desired or higher storage temperatures were expected.

The lowest H_2S formation was observed in the two red wines. These two wines also had the lowest molecular SO_2 values of any wines studied (< 0.13 mg/L), largely because of their high pH values. Furthermore, the molecular SO_2 and free SO_2 values in Table 1 are "apparent" values based on flow injection analysis. FIA and related techniques overestimate molecular and free SO_2 by a factor of 3 on average due to the artifactual measurement of weakly bound

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anthocyanin-bisulfite complexes, and the "true" molecular SO_2 in a survey of commercial red wines was reported to be below 0.2 mg/L (Coelho et al. 2015). This value is below the limit for molecular SO_2 suggested earlier, and thus red wines are expected to be of relatively low concern for H_2S formation during can storage. Alternatively, the low H_2S in the canned red wines could be due to direct effects of polyphenols in these wines on H_2S formation (e.g. by passivation of exposed areas of the can), but this hypothesis was not investigated in the current work.

The mechanism by which SO_2 (either as bisulfite or molecular SO_2) would circumvent the liner is unclear. One hypothesis is that SO_2 penetrates the liner and reaches the metal surface through pores or other liner imperfections. However, based on the results presented, this "pore imperfection hypothesis" seems unlikely for the following reasons:

- If H_2S formation depended only on the initial presence of pores, then H_2S formation with lined and bare coupons should be well correlated across wines, albeit with slower H_2S production for lined coupons. This hypothesis was explicitly tested by comparing H_2S formation under accelerated conditions with lined and bare coupons, and production was poorly correlated, suggesting that certain wines are effectively impeded by liners even if they will react with aluminum (Figure 8).
- Significant increases in H_2S are detected in some wines by 2 months, and in most wines by 4 months (Figure 1). Significant increases in dissolved aluminum Δ[Al], however, are typically not seen until 8 months (Figure 5). This suggests that reactions that allow for H_2S formation occur before the corrosion reactions responsible for Al dissolution.

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582 An alternative hypothesis to the initial presence of liner pores is that SO_2 induces liner
583 failure and H_2S formation. SO_2 gas is reported to degrade polyester coatings in steel, which the
584 authors suggest could be due to the reductive nature of the compound (Ozcan 2002). In the
585 current work, the best predictor of H_2S formation and liner degradation is molecular SO_2. In
586 principle this neutral, volatile form could diffuse through liner coatings as it does through certain
587 polymeric membranes although there are no published studies on diffusion rates of SO_2 through
588 the liner materials in the current study. A complimentary possibility is that the combination of
589 free SO_2 and low pH (which manifests as high molecular SO_2) is responsible for initial liner
590 degradation, after which molecular SO_2 is better able to reach and react with aluminum metal.
591 Initial liner damage would also allow H^+ to reach the metal surface and form H_2 gas, which may
592 further damage the liner through blistering (Vargel 2004). Of these two, the second hypothesis
593 seems better supported by the data considering the sharp increase in H_2S after 4 or 8 months in
594 several wines, which is more compatible with the liner failure explanation as opposed to
595 continuous SO_2 diffusion. The correlation of visible liner damage with Δ[Al] (Figure 4) also
596 supports the conclusion that initial liner damage by SO_2 allows for further corrosive events.
597 In either case, once the liner is sufficiently damaged, the bulk wine will be able to contact
598 the metal surface, and corrosion occurs under acidic, anoxic conditions to generate [Al(III)] and
599 H_2 (Equation 2). [Al(III)] will also be formed by reaction of Al and SO_2, but this will be less
600 important quantitatively; based on stoichiometry and H_2S evolution, < 100 µg/L [Al] will be
601 generated via SO_2 for epoxy lined cans, or <10% of the observed Δ[Al]. In support of this, pH is
602 better correlated with Δ[Al] than molecular and free SO_2, and lower pH has been reported

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603 elsewhere to increase corrosion in beverage cans (Seruga et al. 1994, Stokes et al. 2012,
604 Crouchiere, 2020).

605 The low correlation of chloride and copper with both H_2S formation or Δ[Al] was
606 somewhat surprising, as both components are well known to increase corrosion (Vargel 2004),
607 and can manufacturers generally provide limits for both components. Chloride, for example, is
608 well known to exacerbate aluminum pitting corrosion through formation of $AlCl_4^-$ at the anode
609 (Natishan et al. 2014). However, many of these studies utilize chloride levels comparable to
610 those found in salt water, in the g/L scale (Natishan et al. 2014), exceeding values we observed
611 (< 500 mg/L) in wines. Similarly, copper is reported to facilitate cathodic reactions and
612 corrosion, and could also act as a source of H_2S through copper-sulfhydryl precursors. The lack
613 of correlation may be in part because of the limited number of wines in this study with high
614 levels of copper. Spiking studies to evaluate the effects of copper on canned wine stability would
615 be interesting, with the caveat that Cu salts added to wines are initially more reactive ("labile"),
616 and that they lose reactivity through complexation with sulfhydryls following storage (Clark et
617 al. 2016).

618 Alcohol content did not correlate with either H_2S or Δ[Al] production. Recent work with
619 much higher concentrations of alcohol (up to 85% v/v in hand sanitizer) have reported significant
620 corrosion and liner degradation during can storage, possibly due to plasticizing or dissolution of
621 the liner. However, these effects were not apparent in our study, possibly because the range of
622 alcohol found our table wines (8-14% v/v) is relatively small. Can manufacturers suggest limits
623 for total SO_2 (Coetzee 2021), but we observe no correlation between total SO_2 and H_2S
624 production, indicating that bound SO_2 is not involved in H_2S formation.

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Accelerated shelf-life testing or accelerated aging, in which products are stored at higher temperatures or other extremes, is widely used in the testing of food packaging (Robertson 2005). The test described here is expected to be fit-for-purpose for rapidly testing the suitability of a wine for canning, at least for the epoxy-based liners (BPA epoxy and BPA-NI), for long-term storage up to 8 months at room temperature. H_2S formation at cooler storage temperatures (e.g. 4 °C refrigerator) is expected to be slower than at room temperature. The correlation of H_2S formed during accelerated aging or room temperature storage and storage at cooler temperatures would be of interest to producers and is an appropriate subject for future studies.

Conclusion

Rosé and white wines stored in BPA or BPA-NI epoxy-lined aluminum beverage cans will produce suprathreshold concentrations of H_2S within 8 months, and in some cases in as little as 2 months. Very high production of H_2S is observed within 1 month for acrylic lined cans. H_2S production during long-term storage correlates well with visible liner degradation, but not with increased dissolved aluminum. Results from accelerated aging with spiked wine samples support the hypothesis that H_2S can be formed from reaction of SO_2 with aluminum (Eq 1), and that the extent of H_2S formation is best predicted by molecular SO_2 concentration. To avoid high H_2S (>10 µg/L) following 4-8 months storage in beverage cans, wines should be packaged with molecular SO_2 below 0.4 mg/L for BPA and BPA-NI epoxy cans, and acrylic lined cans should be avoided. The mechanism through which liner failure occurs is unclear but may involve subsequent steps of liner degradation followed by reaction of SO_2 with the aluminum metal. H_2S formation under accelerated storage conditions with lined aluminum coupons is well correlated with H_2S production during long-term storage for epoxy cans, and it is expected that this assay

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will be useful to winemakers for predicting the suitability of a wine for can storage or evaluating the effects of wine components. More generally, the accelerated aging approach described here could be extended to predicting the compatibility of aluminum cans with other corrosive beverages (e.g. sour beers, kombucha), and thus has the potential to increase the effective use of beverage cans as a more sustainable alternative for single-use packaging.

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Table 1 Initial composition of wines used for accelerated and long-term aging. In the column titled closure type, "C" corresponds to cork while "SC" corresponds to screw cap for each wine in bottle. Molecular SO_2 was calculated from pH and free SO_2 using ethanol and temperature corrected pK_a values (Coelho et al. 2015)

Code	Varietal and Style	Closure Type	Country of Origin	pH	TA (g/L)	Alcohol (%v/v)	SO_2 (mg/L)			RS (g/L)	Acids (g/L)			Al (mg/L)	Cu (mg/L)	Cl- (mg/L)
							Free	Total	Mol		Malic	Lactic	Acetic			
Ro1	Rosé blend	C	USA	3.37	7.2	9.59	19	111	0.64	36.8	2.65	0.35	0.23	1.1	0.05	288
Ro2	Rosé blend	SC	FR	3.41	6.4	11.0	19	89	0.62	0.9	2	0.6	0.22	0.7	0.06	32.1
R1	Red blend	C	USA	3.92	6.4	13.1	17	41	0.19	3.7	0.2	2.1	0.52	0.7	0.05	290
R2	Red blend	C	USA	3.91	6.1	13.2	11	36	0.13	13	0.3	1.9	0.45	1.2	0.39	326
W1	White blend	SC	USA	3.31	7	12.8	26	113	1.15	5	2.8	0	0.14	1.1	0.15	163
W2	Riesling (white)	SC	GER	3.00	9.1	8.57	29	133	2.1	39	2.89	0.27	0.31	0.7	0.07	78.5
W3	Chard. (white)	C	USA	3.57	6.7	12.7	22	142	0.54	8	0.9	2.1	0.44	1.5	0.06	442
W4	Chard. (white)	SC	AUS	3.52	5.5	12.8	31	129	0.86	5	0	2.6	0.35	1.3	0.06	313
W5	White blend	SC	USA	2.9	8.3	11.3	24	119	2.4	65	2.56	0.16	0.2	0.7	0.09	117
W6	Riesling (white)	SC	USA	3.05	8.2	11.3	28	104	2.0	15	2.4	0.2	0.51	2.1	0.11	122

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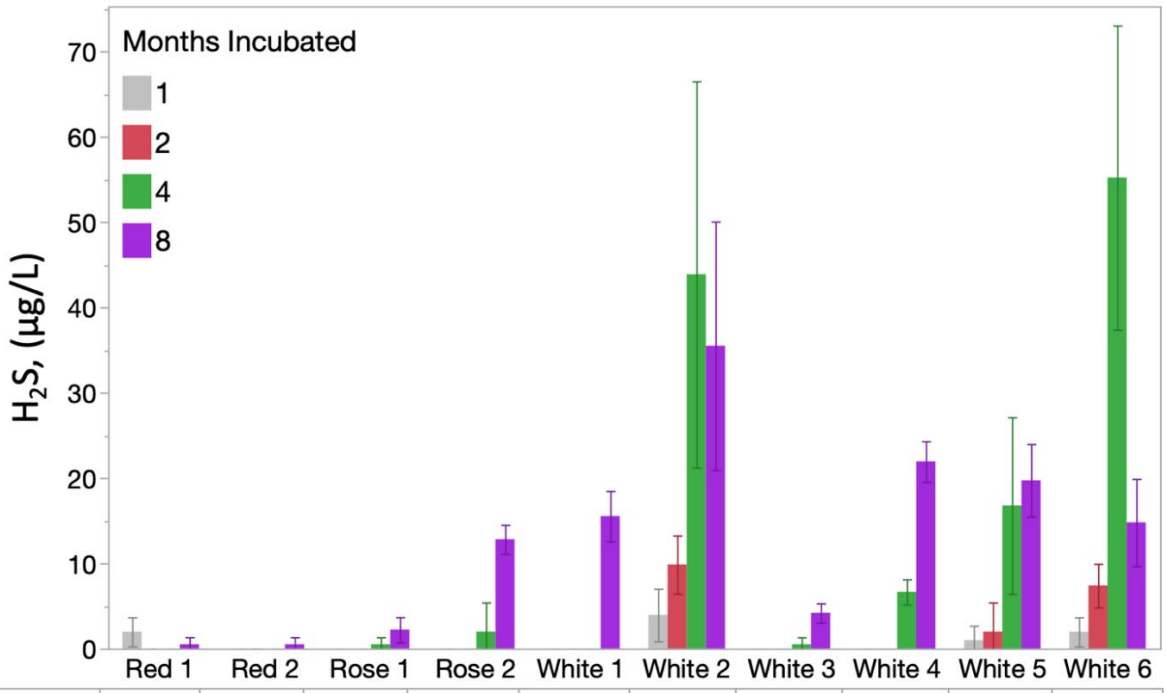

	Red 1	Red 2	Rose 1	Rose 2	White 1	White 2	White 3	White 4	White 5	White 6
H_2S, Epoxy Lined Cans (µg/L)	0.4	0.3	1.4	7.4	8.0	39.7	2.3	14.3	18.3	35
H_2S, Glass Storage (µg/L)	n.d.	5.2	n.d.	2.2	n.d.	2.0	n.d.	n.d.	n.d.	n.d.

Figure 1 H_2S as a function of storage time (1, 2, 4, or 8 months) for ten commercial wines packaged in replicate BPA-epoxy lined cans (n=3 per time point for each wine; error bars represent 1 StDev). Average H_2S of 4 and 8 months for each wine stored in BPA-epoxy cans or stored in glass are reported below the bar chart.

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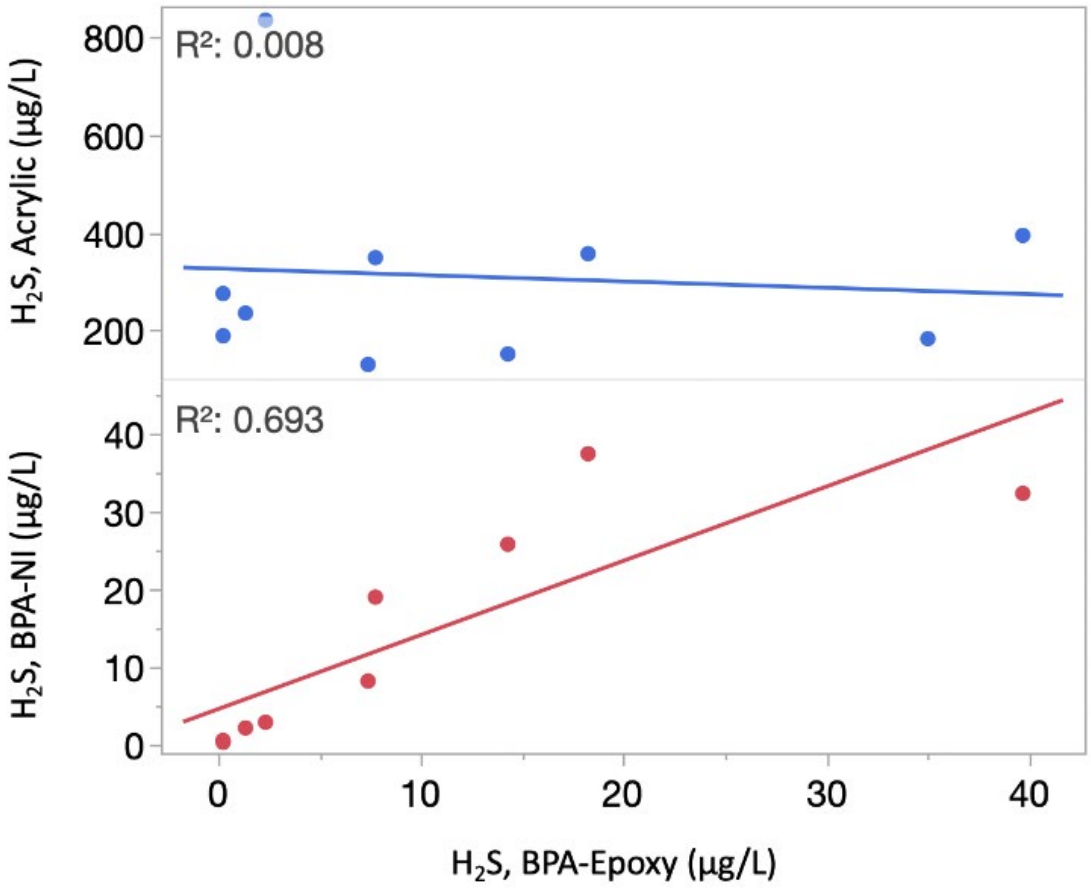

769
770 **Figure 2** Linear regressions of H_2S for wines stored in BPA-epoxy vs acrylic (top) and BPA-epoxy vs.
771 BPA-NI (bottom) lined cans. Each point represents an average H_2S value measured following 4 and 8
772 months (n=3 for each time point, n=6 total)
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Figure 3 Representative images of cans scored with a '0' (left, undamaged BPA-epoxy) and '5' (right, badly damaged acrylic).

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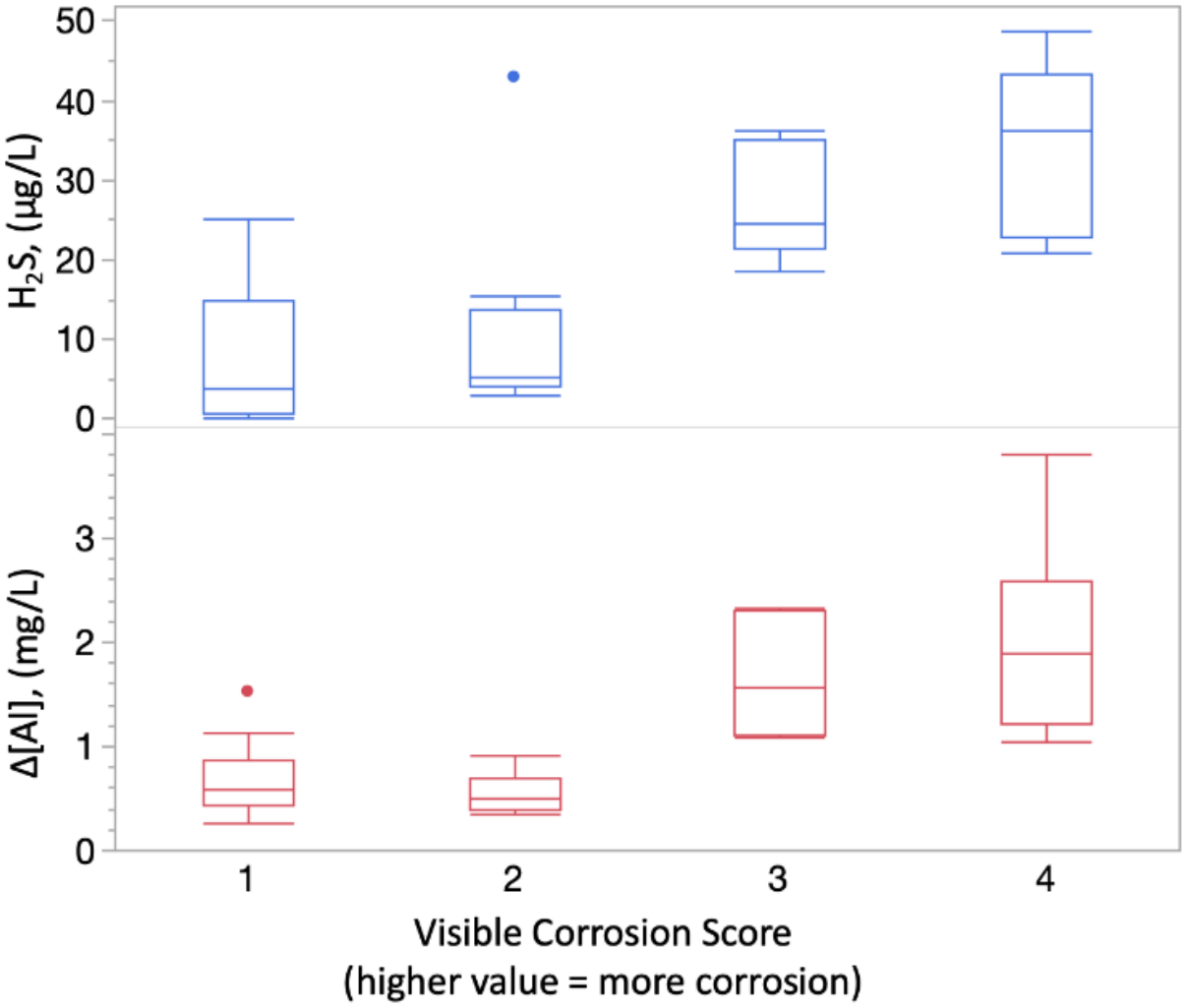

Figure 4 Change in dissolved aluminum (Δ[Al]) and H_2S for BPA and BPA-NI epoxy cans scored based on visible damage to liner (0 = no damage, 5 = delamination, maximum damage; no epoxy samples had a score of 5). Both Δ[Al] and H_2S were significantly correlated with visible damage (Spearman's rank order test; $p < 0.001$).

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823 Figure 5
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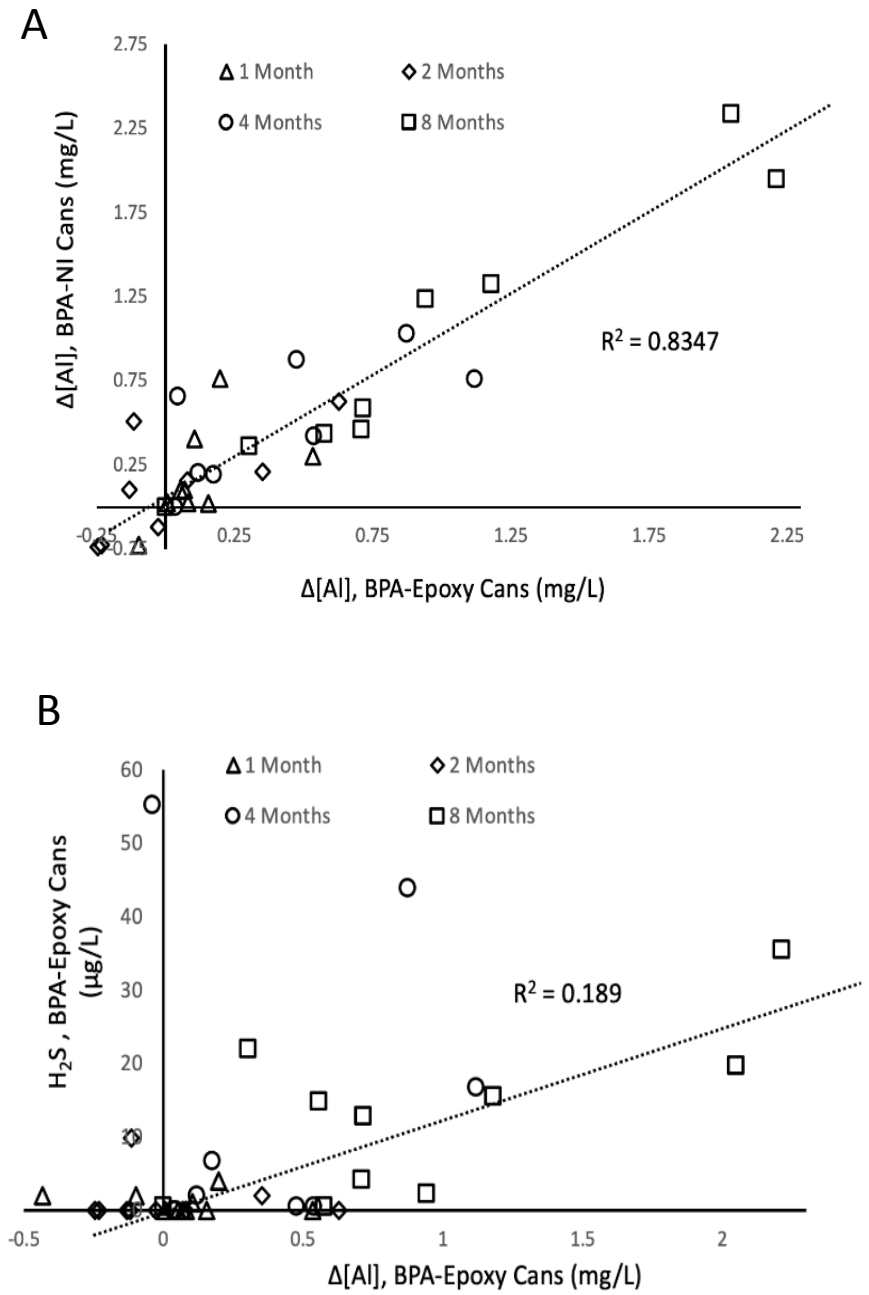

825
826
827 **Figure 5** a) Change in dissolved aluminum (Δ[Al]) in BPA-NI epoxy vs. BPA epoxy cans across all
828 storage time points (1, 2, 4, and 8 months) and wines; b) Δ[Al]) vs H_2S (µg/L) for BPA epoxy cans
829 across all storage time points. Each point represents an average of three can replicates.
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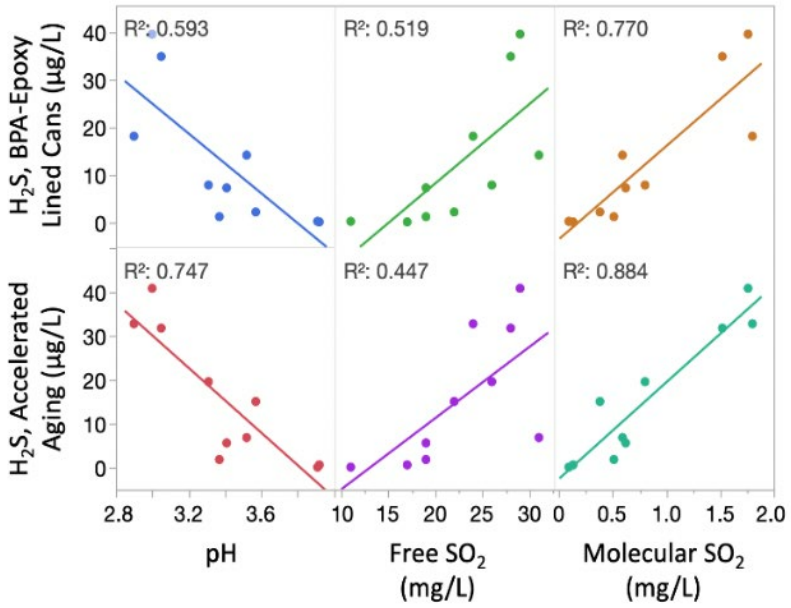

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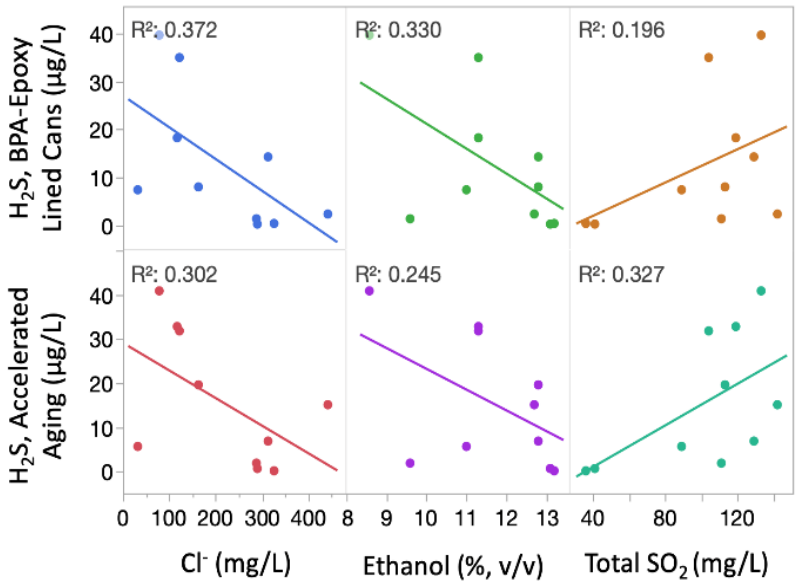

Figure 6 a) Linear regressions of H_2S formation and initial wine composition (pH, Free SO_2, and Molecular SO_2) following a long-term storage in BPA-epoxy lined cans (average of 4 and 8 months) or under accelerated aging conditions with BPA-epoxy lined coupons (average after 3 d and 14 d at 50 °C); b) Linear regressions of H_2S formation and initial wine composition (chloride, ethanol, and total SO_2) following a long-term storage in BPA-epoxy lined cans (average of 4 and 8 months) or under accelerated aging conditions with BPA-epoxy lined coupons (average after 3 d and 14 d at 50 °C).

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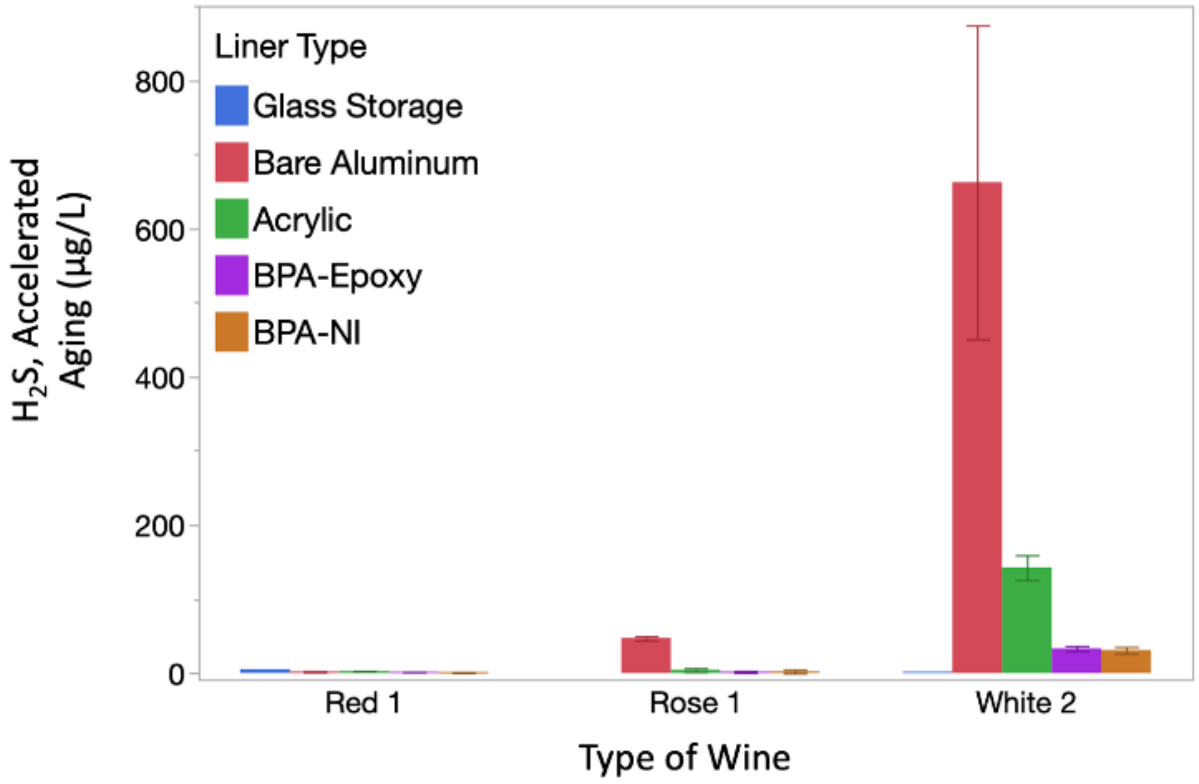

Figure 7 H_2S formation under accelerated aging conditions (3 d, 50 °C) for a representative red, rosé, and white wine using either no coupon (glass control), acrylic-lined coupons, BPA-Epoxy-lined coupons, BPA-NI epoxy lined coupons, or bare aluminum coupons. Three replicates were run per trial, and error bars represent 1 standard error.

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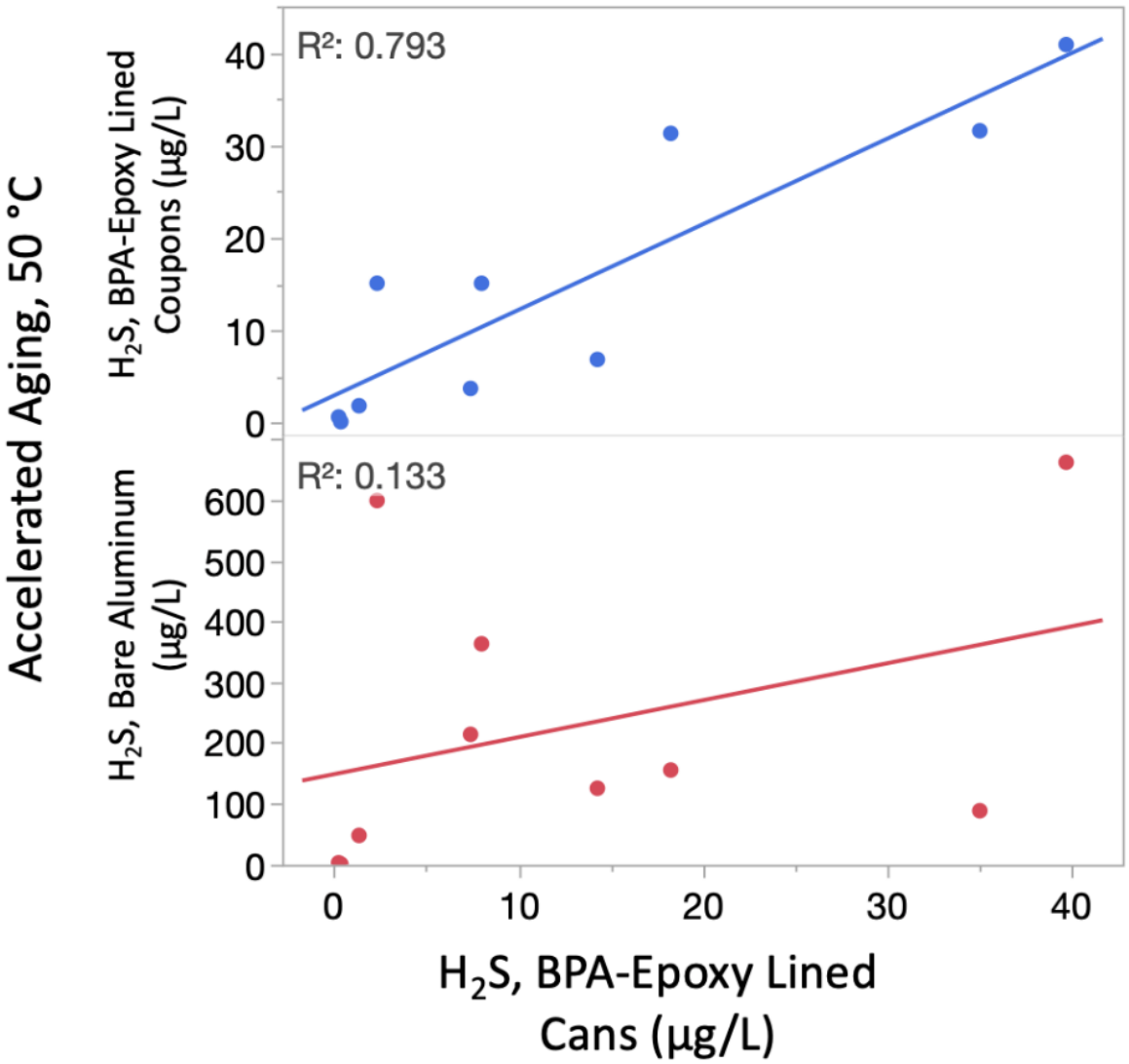

Figure 8 Linear regressions of H_2S formation during long-term storage in BPA-epoxy lined cans (average of 4 and 8 months) vs either (top) accelerated aging in the presence of BPA-epoxy lined coupons or (bottom) bare aluminum coupons.

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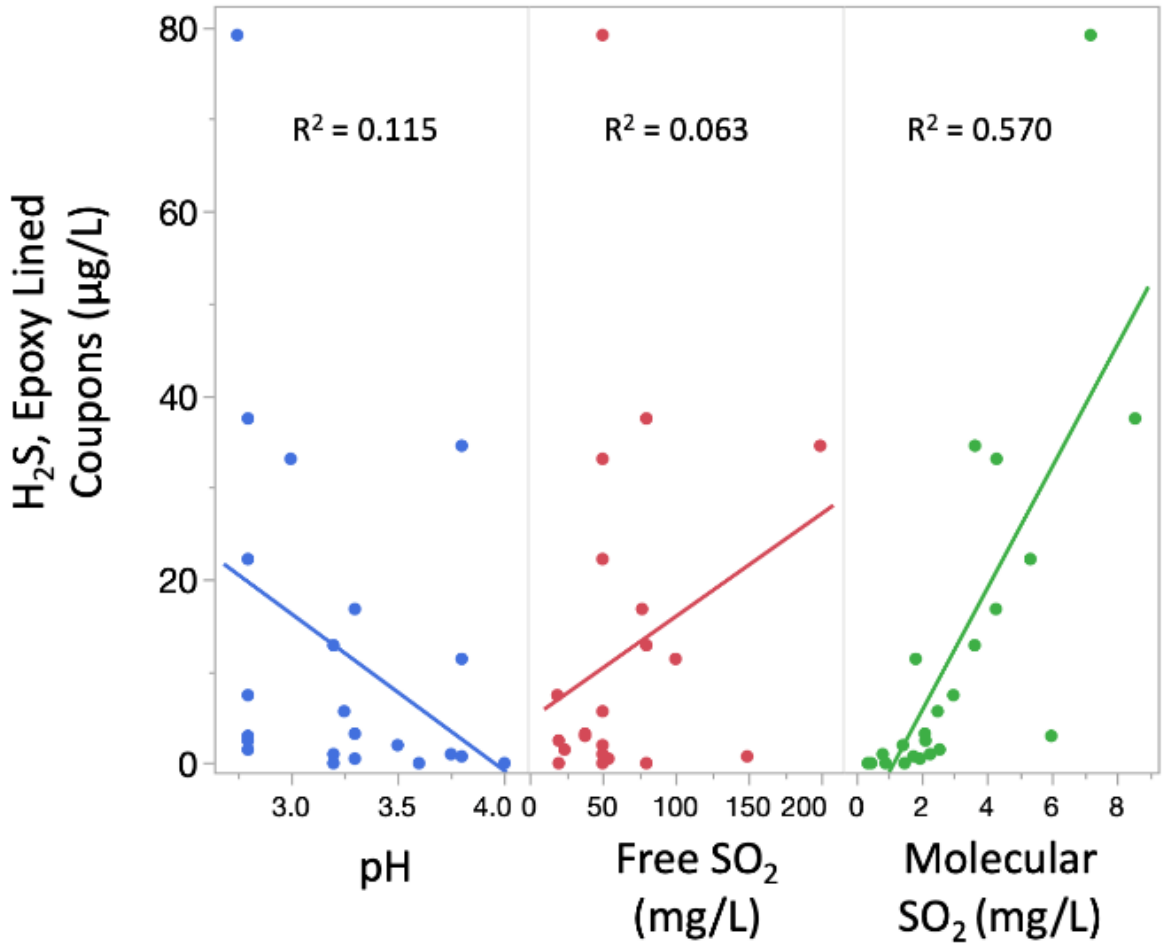

Figure 9 Linear regressions of H_2S formation in model wine solutions as a function of molecular SO_2 (calculated at 20 ° C), pH, and free SO_2 for spiked wines stored under accelerated aging conditions (3 d at 50°C with BPA-epoxy coated coupons.

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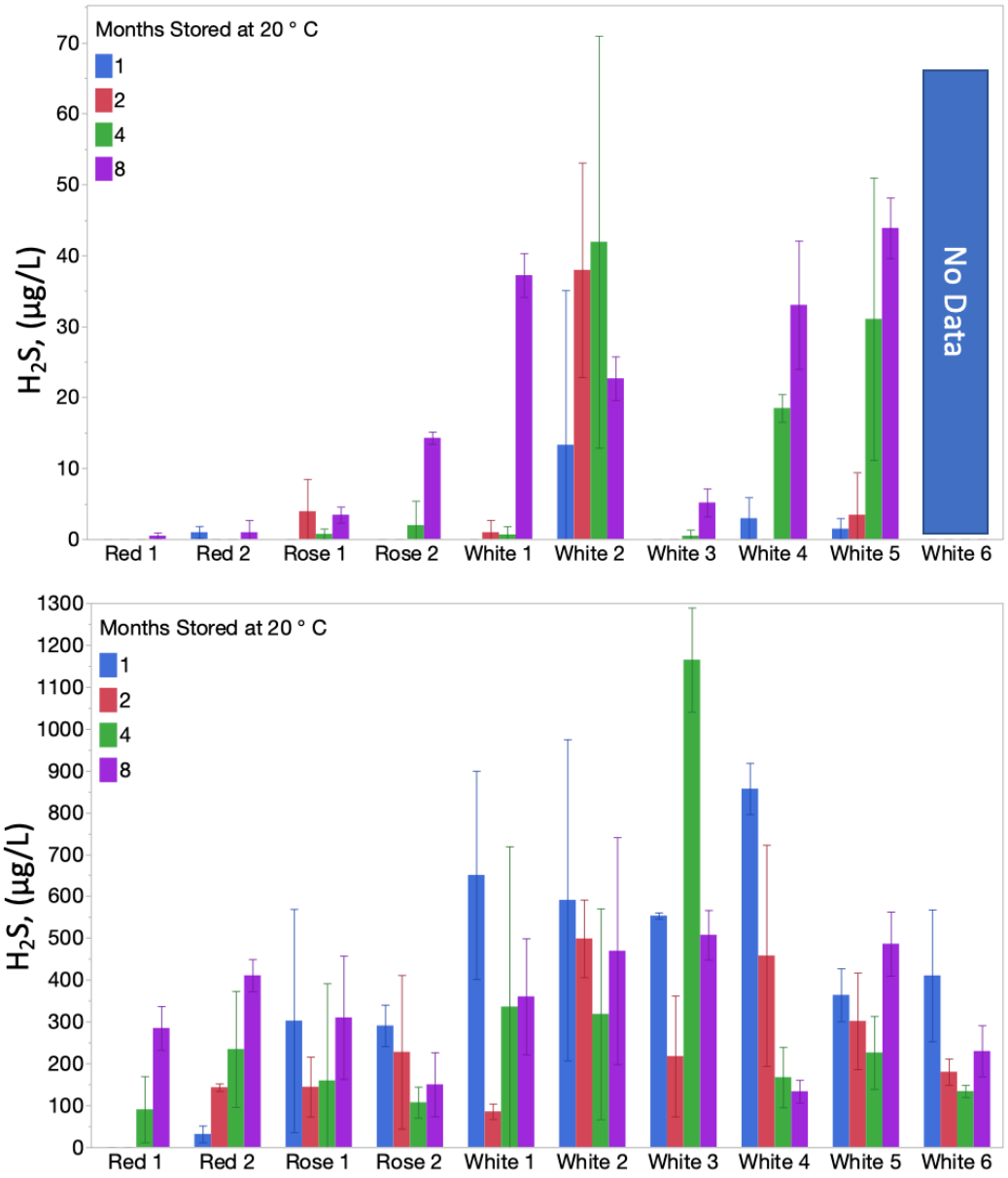

Supplemental Figure 1 H_2S produced after 1, 2, 4, and 8 months storage in BPA-NI coated cans (above), and acrylic coated cans (below).

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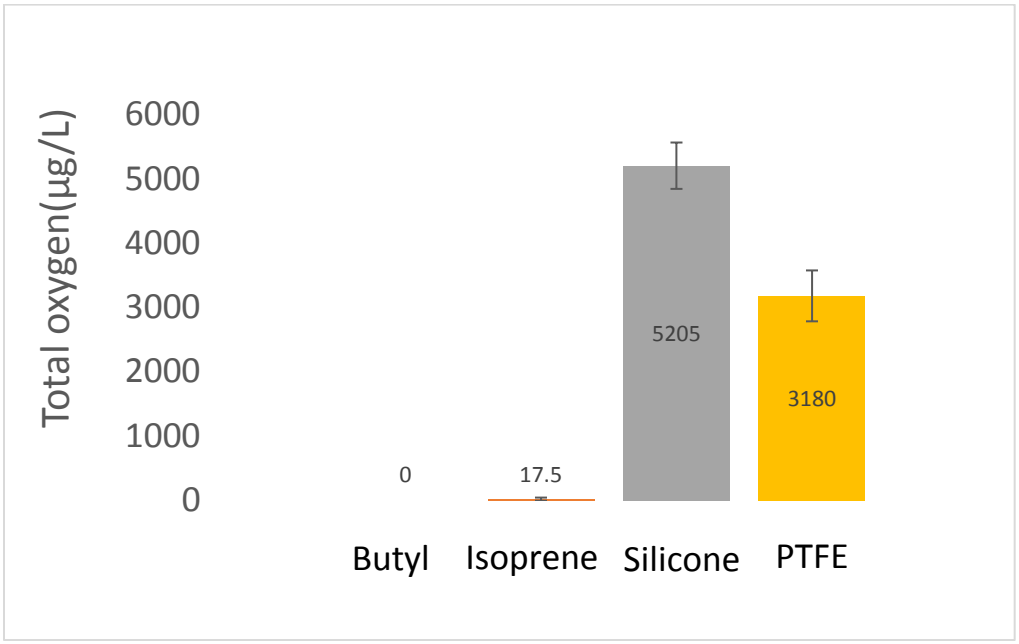

860
861 **Supplemental Figure 2** Total oxygen ingress during storage of water in crimp capped vials at 40 °C for
862 7 days, as a function of septum material
863

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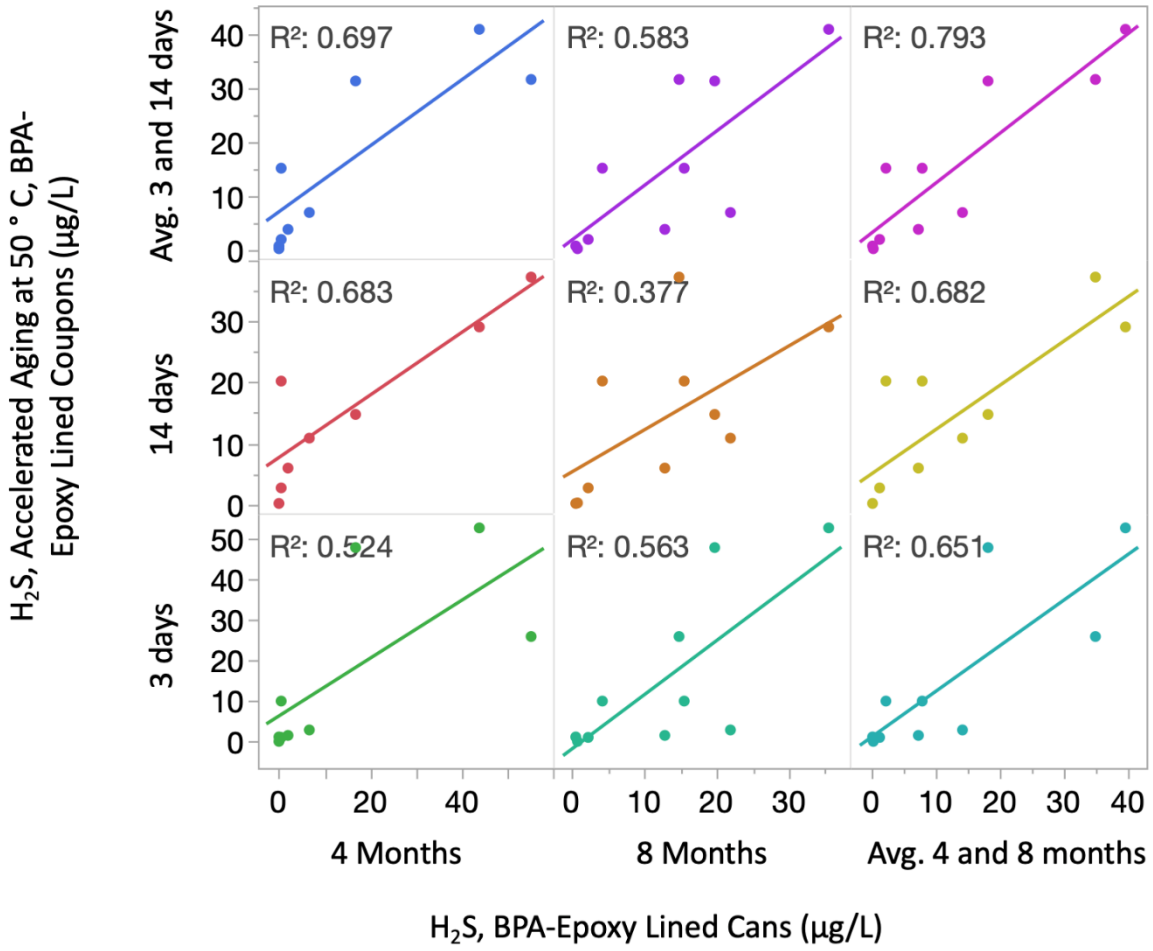

Supplementary Figure 3 Regression plots of H_2S formed under accelerated aging conditions (3 d, 14 d, or average of 3 and 14 d) vs. H_2S formed during long term aging (4 mo, 8 mo, or average of 4 and 8 mo). Accelerated aging conditions used BPA epoxy coupons at 50 °C, and long-term aging used BPA epoxy cans. Each point represents one of ten commercial wine, prepared in triplicate.

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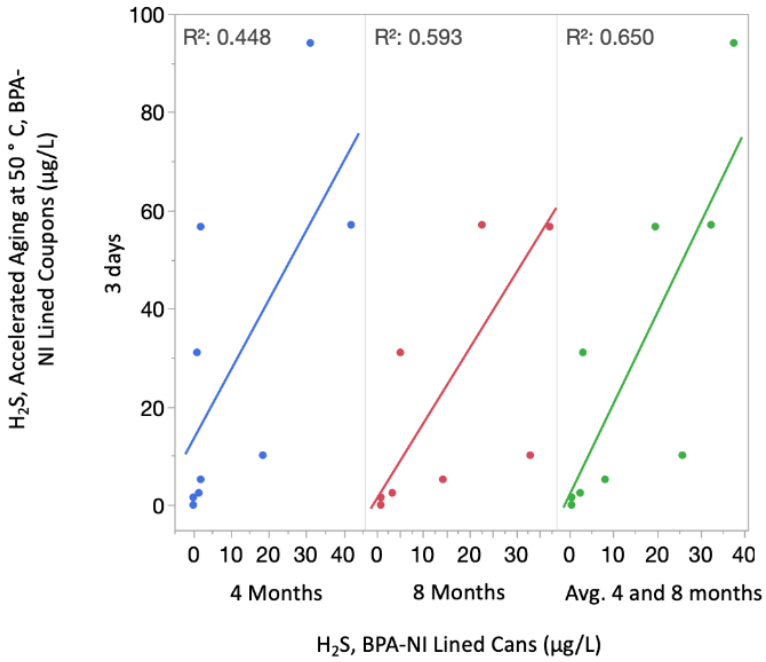

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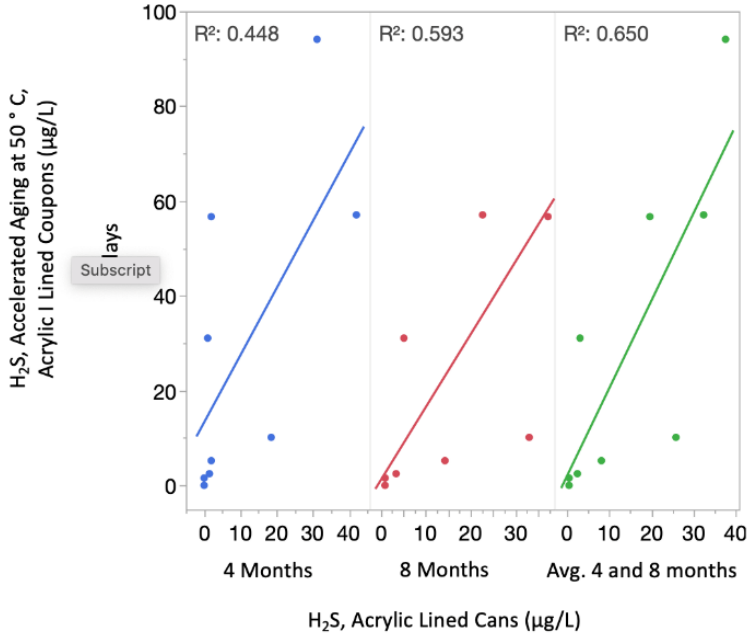

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876 **Supplementary Figure 4** Regression plots of H_2S formed under 3d accelerated aging conditions vs.
877 H_2S formed during long term aging (4 mo, 8 mo, or average of 4 and 8 mo). The top plot used BPA-NI
878 epoxy lined cans and coupons, and the bottom plot used acrylic lined cans and coupons. Each point
879 represents a commercial wine, prepared in triplicate.

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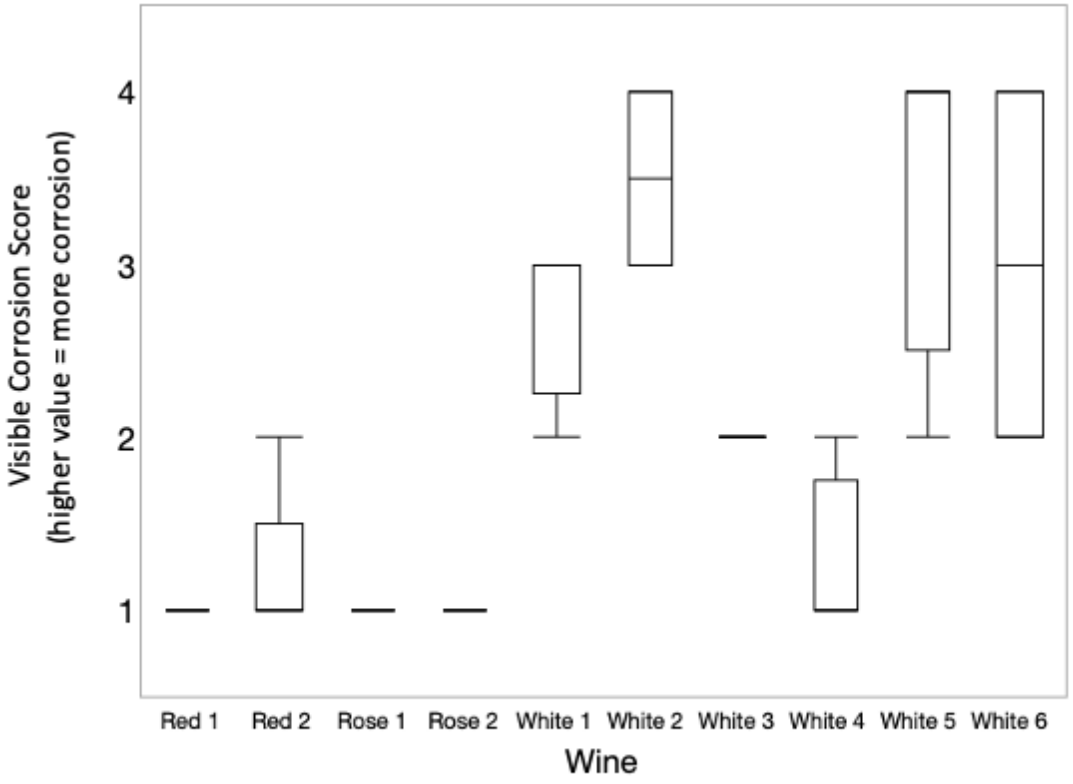

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881 **Supplementary Figure 5** Corrosion scores for commercial wines stored in BPA-epoxy and BPA-NI
882 epoxy lined cans after 8 months of storage. For each wine, n = 3 or n = 6 depending on availability of
883 cans.
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