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

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Abstract

Background and goals
Wines in aluminum beverage cans ("canned wines") are a rapidly growing packaging segment due to several factors, including convenience and sustainability. However, canned wines have higher concentrations of hydrogen sulfide (H_2S; "rotten egg") than wines in glass packaging. We 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 glass or in aluminum beverage cans with one of three liners for up to 32 weeks. Wines stored in glass showed 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 eight weeks. Wines stored in cans lined with bisphenol A (BPA) epoxy produced less H_2S (maximum = 51.8 µg/L, median = 11.8 µg/L after 32 weeks), with comparable performance observed for cans with 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°C, up to 14 days, 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; 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 of up to eight months. The accelerated aging approach described in this work may be applicable to other corrosive beverages.

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

Introduction

The global value of wines packaged in aluminum beverage cans ("canned wines") is projected to increase considerably between 2021 and 2028, from $235.7 million to $570 million (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 use (Williams et al. 2019). In addition, aluminum is recycled at a higher rate than either glass or polyethylene terephthalate (PET), which appeals to consumers concerned about packaging waste (US EPA 2020).

Compared with many other types of wine packaging (e.g., glass bottles 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 (Stokes and Barics 2013, Scrimgeour et al. 2019, Allison et al 2020, Coetzee 2021, Thompson-Witrick et al. 2021). A major concern for winemakers with any packaging is oxygen (O_2) exposure and subsequent wine oxidation (Revi et al. 2014, Crouvisier-Urion et al. 2018). However, the excellent barrier properties of a can's double seam allow only trivial O_2 exposure to a beverage, assuming the initial total package O_2 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 storage period (Wisk et al. 1987). Assuming an air O_2 content of 21%, this amount of air equates to an ingress rate of 0.1 mg/L O_2 per year. This ingress rate is lower than the rates reported for glass bottles under a range of closures (Dimkou et al. 2011) and would result in a negligible decrease of total sulfur dioxide (SO_2, <0.5 mg/L per year) based on the expected 2:1 molar stoichiometry of total SO_2 loss versus O_2 consumption in wine (Danilewicz and Standing 2018).

Unlike oxidation, 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 hydrogen sulfide (H_2S, "rotten egg" aroma) in canned wines averaged >10-fold higher than concentrations in glass-packaged wines (13.5 versus 1.1 µg/L), with all canned wines containing H_2S above the sensory threshold (~1 µg/L, Siebert et al. 2010). Multiple nonvolatile precursors capable of releasing H_2S under anoxic 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 O_2 exclusion, as has been observed with low-O_2 ingress screwcaps 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. Indeed, a 1937 study 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 focused on 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:

$$2\ Al^0_{(s)} + SO_{2\ (aq)} + 6\ H^+_{\ (aq)} \rightarrow\ 2\ Al^{3+}_{\ (aq)} + H_2S_{(g)} + 2\ H_2O \qquad \text{(Eq. 1)}$$
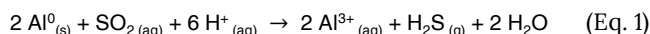
This reaction is thermodynamically plausible and is cited in a patent (Stokes and Barics 2013) and technical bulletin (Coetzee 2021), although the peer-reviewed literature lacks confirmation of its occurrence. These publications stated that limiting SO_2 in canned wines was necessary to prevent H_2S formation by the reaction proposed in Equation 1. For example, one technical bulletin recommends the following limits for canned wines: free SO_2 < 20 mg/L, total SO_2 < 75 mg/L, and molecular SO_2 < 0.2 mg/L (Coetzee 2021). That bulletin also recommended limits for other components such as pH, alcohol, dissolved copper (Cu), and dissolved chloride (Cl), although no references or peer-reviewed literature are provided as justification.

Although the reaction of SO_2 with aluminum is not well studied, considerable research exists on corrosion of aluminum in the aqueous, acidic conditions typical of most canned 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 systems with a low pH and a low O_2 level (both 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.

$$2\ Al^0_{(s)} + 6\ H^+_{\ (aq)} \rightarrow 2\ Al^{3+}_{\ (aq)} + 3\ H_{2\ (g)} \qquad \text{(Eq. 2)}$$
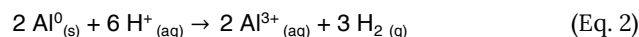
These reactions are accelerated at lower pH and in the presence of elements such as Cu (both ions in solution and impurities in aluminum alloys), which will integrate into aluminum to facilitate cathodic reactions, or Cl, which forms $AlCl_4^-$ and facilitates the anodic reaction (Vargel 2004). These corrosion reactions can lead to leaking and loss of the hermetic seal in unlined beverage cans, and the resulting increase in dissolved aluminum, [Al], could affect flavor, cause hazes, and adversely affect human health (Tariba 2011, Klotz et al. 2017).

To slow corrosion reactions like that shown in Equation 2, beverage-can manufacturers coat the can interior with a thin (1 to 10 µm) nonporous 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 use monomers other than BPA (e.g., bisphenol F) (Soto et al. 2017).

Peer-reviewed literature on the effects of SO_2 or other components on corrosion, H_2S formation, or other unwanted reactions during beverage-can storage is nonexistent for wine and limited for other beverages. One group observed modest variation in the increase in [Al] (0.3 to 1.2 mg/L) among seven carbonated sodas over 12 months in storage, which the authors argued was the result of the higher citric acid level and lower pH of certain samples (Seruga et al. 1994). Another study observed comparable levels of [Al] for seven of nine drinks evaluated, although two of the drinks showed much higher [Al] concentrations (up to 74 mg/L after 29 months). The authors again credited the greater [Al] concentration of one beverage (juice) to its higher citric acid content. One challenge with interpreting 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 that evaluated the canning of ethanol-based hand sanitizers using two liner types (epoxy and BPA-NI). The authors concluded that high ethanol content (75 to 85% v/v) causes rapid liner degradation and corrosion compared to other sanitizer components (0.125% H_2O_2 and 1.45% glycerol). Another report (Soares et al. 2019) used a combination of [Al] and electrochemical approaches to evaluate the effects of various concentrations of Cu and Cl⁻ in model beverage systems on corrosion; they concluded that liner variability was more important than composition. However, the validity of extending these reports to commercial wines is uncertain.

The poor documentation in the peer-reviewed literature of the effects of liner type and wine composition on can corrosion and H_2S formation creates a challenge for meeting producer and consumer interest in expanding production of beverages packaged in aluminum cans. In this work, we

report a study on the formation of H$_2$S in canned wines as a function of liner type and wine composition in comparison to glass after up to eight months in storage. In addition, we develop and describe a convenient accelerated aging assay (<14 days) that uses lined aluminum coupons, and we validate the accelerated assay against long-term storage studies for evaluating the wine components likely responsible for H$_2$S formation. This work is immediately useful for winemakers as a resource for quality winemaking in cans and could also potentially be applied to to any other beverage stored in aluminum beverage cans.

Materials and Methods

Materials and chemical reagents

Liquid nitrogen (LN$_2$) and nitrogen gas (ultra-high purity) were obtained from Airgas. A 500-mL LN$_2$ sprayer was obtained from US Solid. Headspace vials (30 mm × 60 mm, 27 mL), 20-mm butyl rubber septa, 20-mm tear-away crimp seals, and a 20-mm hand crimper were all obtained from Supelco (product codes 27298, Z166065, 27016, and 33280-U, respectively). A 5- to 25-mL bottle-top dispenser was obtained from VWR (product code 82017-768). A coated, clear 1000-mL glass bottle with septa port was obtained from Ankom Technology. A Surebonder electric glue skillet and Surebonder B-2001 hot glue pellets were obtained from Amazon.

Double-side-coated sheets of 3004 aluminum alloy 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-μm coating thickness).

Can ends (5000 series alloy, BPA Epoxy 202LOE B64 style; American Canning) were obtained from the same industry collaborator. The Oktober MK16 can seamer was obtained from Oktober Design. A 22.7-L water cooler was obtained from a local Walmart. An aeration-oxidation apparatus was obtained from GW Kent. Gastec detection tubes (Gastec International) used for analyses of H$_2$S (4LT and 4LL) and SO$_2$ (5L) were purchased from Airgas and Grainger.

Ethanol (EtOH), 70% v/v, was purchased from Koptec. L-(+)-tartaric acid (99%) was purchased from Acros Organics. Sodium hydroxide pellets were obtained from Fischer Scientific. Sodium sulfide nonahydrate (Na$_2$S · 9H$_2$O, 99%) was purchased from Beantown Chemical. Acetaldehyde (CH$_3$CHO, 99%) was purchased from Alfa Aesar. Potassium metabisulfite (K$_2$S$_2$O$_5$, 99%) was purchased from Fisher Scientific. Perchloric (70%) and nitric acid (70%) were obtained from GFS and Fisher Scientific, respectively, and redistilled into Teflon vessels 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 Cu and [Al] were analyzed at a local facility (USDA-ARS Holley Center, Ithaca, NY) using a Thermo Scientific iCAP 6500 series system for inductively coupled plasma-optical emission spectroscopy (ICP-OES) and a protocol described in a later section. Cl was measured with a SympHony Combination Chloride Electrode (VWR International) using the manufacturer's protocol. All other wine analyses were performed by

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 screwcap for each wine in bottle. Molecular SO$_2$ was calculated from pH and free SO$_2$ using ethanol and temperature corrected acid dissociation constant values (pK$_a$) (Coelho et al. 2015). TA, titratable acidity; RS, residual sugar.

Code	Varietal and style	Closure type	Country of origin	pH	TA (g/L)	Alcohol (%v/v)	SO₂ (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	France	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	Germany	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	Australia	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

the Cornell Craft Beverage Analytical Laboratory (Geneva, NY) using standard protocols: Alcohol by volume was determined by OenoFoss (Foss), free and total SO_2 were determined by flow injection (FIAstar 5000 Analyzer; Foss), titratable acidity (TA) was measured by autotitration (Metrohm 862 Compact Titrator), pH was measured on a Fisher Scientific Accumet Excel XL25 dual-channel pH/ion meter, and fructose + glucose was measured enzymatically (Randox RX Monaco). Molecular SO_2 was manually calculated with the following equation using acid dissociation constant values (pK_a) values adjusted for alcohol as described by Coelho et al. 2015:

$$\text{Molecular } SO_2 = \frac{\text{Free } SO_2}{1+10^{pH-pKa}} \qquad \text{(Eq. 3)}$$

Real-time storage stability study

For each wine, 15 L wine (twenty 750-mL bottles or ten 1.5-L bottles) was 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 the O_2 concentration was <0.1 mg/L (Fibox 3 LCD trace O_2 meter w/ DP-PSt6 oxygen dipping probe; Presens). A steady flow of nitrogen gas was introduced to backfill the cooler during can filling to prevent O_2 pickup.

Can bodies (355 mL; 3004 alloy) coated with one of three liner types—BPA epoxy, Gen II BPA-NI epoxy, or acrylic—and lids (5000 series alloy, BPA Epoxy 202LOE B64 style; American Canning) were rinsed with 70% ethanol before use. Immediately prior to filling, a few mL of LN_2 was added to the can body to expel O_2 and retain can pressure. Once the LN_2 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 LN_2 were added to remove headspace O_2, and the can was immediately topped with a lid and seamed on a manual double seamer (MK16 seamer; Oktober Design). Seam quality was validated using an industry-standard tear-down protocol (first-operation seam thickness, 1.88 to 1.98 mm; second-operation seam thickness, 1.07 to 1.19 mm; cover hook length, 1.34 to 1.65 mm; body hook length, 1.40 to 1.91 mm). Total package O_2 (TPO; sum of O_2 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 O_2 concentration of the liquid with a dipping probe. Using this protocol, TPO was determined to be <1.5 mg O_2/L for the 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 (one, two, four, or eight months of storage; three storage replicates for each wine and each time point). The longest time point (eight months) was selected to correspond to the minimum shelf life desired by regional canned wine producers (personal communications). Due to a shortage of BPA-NI epoxy cans, wine 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). The unopened control wines differed in their closures (screwcap versus 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) followed by purging with two to three drops of LN_2 and dispensing of 25 mL wine. Vials were then lightly capped with 20-mm butyl rubber septa to allow excess LN_2 to dissipate and to prevent cracking of the vials due to excess pressure (typically for ~10 to 15 sec). Vials were then sealed with a 20-mm aluminum metal crimp cap and stored at elevated temperature prior to H_2S measurement. Further information on lined coupon preparation, wine dispensing, and temperature storage conditions are provided below.

A two-necked glass bottle (1000 mL, coated, clear with septa port; Ankom Technology) was used for deoxygenating and dispensing wine samples. The side-arm of the bottle was fitted with a screwcap septum closure. Wine (20°C; 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 noninvasive PreSens sensor spots (SP-PSt6). Following deoxygenation, a small amount of LN_2 was added, and the bottle was capped with an adjustable 5- to 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 overpressure of the dispenser. Prior to the loading of sample vials, 75 mL 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) were filled with deoxygenated water using the protocol above, closed with one of four different septum materials (butyl rubber, silicone, PTFE/silicone, or isoprene), and stored for up to seven days at 40°C. Dissolved O_2 was measured using a PtS6 optical SMA attached to a Fibox 3 LCD Trace dissolved O_2 meter (PreSens). Butyl rubber septa were determined to provide the best performance in limiting O_2 ingress. The TPO for samples sealed with butyl rubber septa at 50°C was then determined using a similar experiment, except that dissolved O_2 was measured at regular intervals for up to 14 days (n = 10 replicates).

Coated aluminum coupons (1 cm × 4.5 cm) were cut with shears from sheets of coated 3000-series aluminum alloy (total thickness = 18 μm; coating thickness = 3.2 μm) provided by an industry collaborator. The coatings had the same composition as those used in the beverage cans (BPA epoxy, BPA-NI epoxy, or acrylic). Following cutting, the edg-

es of each coupon consisted of uncoated aluminum. These bare edges were sealed with an ethyl vinyl acetate (EVA) hot melt glue (B-2001 pellets; Surebonder) and allowed to air dry (~30 sec). EVA was chosen due to ease of application and nonreactivity with H$_2$S, as discussed in the Results.

To evaluate the ability of hot-melt glue to prevent formation of H$_2$S by wine-aluminum contact, unlined aluminum coupons were either coated entirely in hot-melt glue or left uncoated as controls. To confirm that the hot-melt glue did not react with evolved H$_2$S, unlined aluminum coupons were prepared with and without edges coated with hot-melt glue. The coupons were then incubated in a white wine with undetectable initial H$_2$S for three days at 50°C under the accelerated-aging conditions described above, after which H$_2$S was measured using gas detection tubes (GDT).

Characterization of stored wines: H$_2$S, visual inspection, and [Al]

H$_2$S was measured using a modified aeration-oxidation (A-O) apparatus with quantitation by GDT (Allison et al. 2022). An H$_2$S GDT was attached in series between the receiver flask of the A-O apparatus and the vacuum source. During an analysis, the sample was aspirated, resulting in a stain forming on the GDT via reaction of H$_2$S with a metal salt in the tube. The length of stain on the GDT is proportional to the original H$_2$S 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$_2$S GDT. The calibration was performed using five standards over a range of 0 to 86 µg/L for 4LT tubes and 0 to 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$_2$S samples, analyses were initially performed with 10 mL of sample, which could subsequently be increased to up to 60 mL, depending on H$_2$S concentration. The methodological detection limit was ~1 µg/L.

For visual inspection of can corrosion, can tops and bottoms were cut with a Gryphon C-40 band saw (Gryphon Corp.), then cut lengthwise with scissors. Can samples were scored on a 0 to 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.

[Al] was measured via ICP-OES. Wine (2 mL) was pipetted into glass vials and allowed to evaporate to dryness at 60°C for three days. Dried samples were digested via the following procedure: adding 60:40 HNO$_3$:HClO$_4$ (3 mL) in a Pyrex glass tube, storing overnight at room temperature, and heating the samples at 70 to 120°C for two hours and then at 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 was raised to 190°C for 10 min, and the samples were 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 were pre-pared in 2% HClO$_4$. Aluminum was measured at 396.152 nm in axial view mode by ICP-OES (Thermo iCAP 6500 series; Thermo Scientific).

Validation of accelerated storage stability study

Different bottles of the same commercial wines and 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 three or 14 days 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$_2$S was measured in all samples by GDT assay. Accelerated aging was also evaluated using unlined (bare) aluminum 3000-series alloy coupons (1 cm × 4.5 cm) for a subset of wine samples.

Effects of pH, free SO$_2$, ethanol, and molecular SO$_2$ on H$_2$S 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$_2$S 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$_2$S among the white wines studied. To achieve different ethanol levels, 70% ethanol or deionized water (DI) was added to the base wine such 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 six different levels (2.75, 3, 3.25, 3.5, 3.75, and 4). The second experiment contained two levels of alcohol by volume (8 and 18%) and three levels of pH (2.9, 3.3, and 3.8); free SO$_2$ varied from 19 to 368 mg/L to create two levels of molecular SO$_2$. The final 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.). Analysis of variance (α = 0.05) was used to evaluate the effects of storage time, liner, and wine on H$_2$S production. Multiple linear regressions were used to evaluate correlations between wine composition and H$_2$S production, [Al], and liner degradation. Linear regressions ($p < 0.05$) were used to evaluate the agreement between room temperature and accelerated storage conditions.

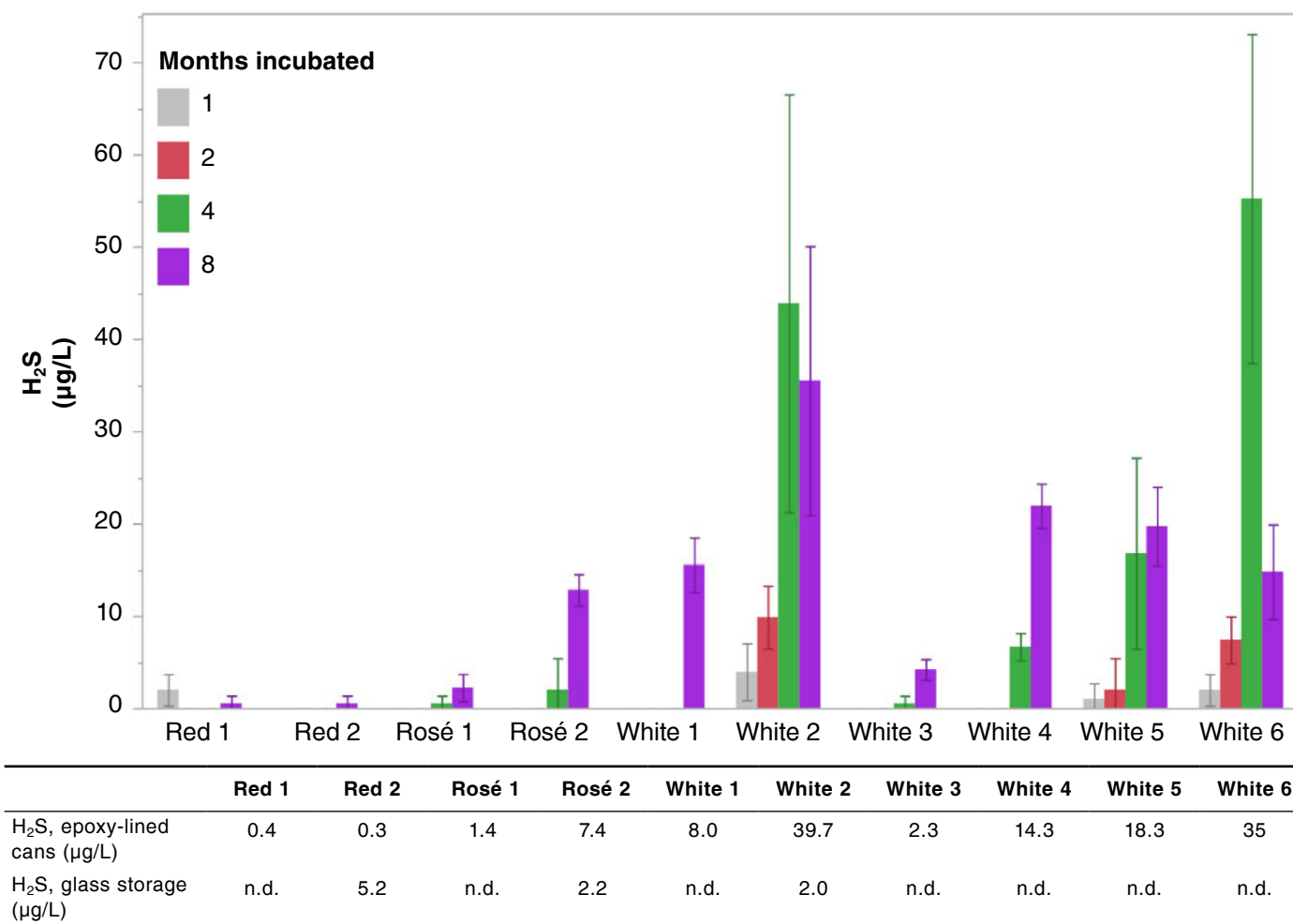# Results

H₂S in canned wines versus glass: Effects of storage time and liner type

Ten glass-packaged commercial wines were repackaged in cans with one of three liner types (BPA epoxy, BPA-NI epoxy, and acrylic). H_2S was measured after one, two, four, and eight months of storage, with H_2S produced after eight months in wines stored in their original glass packaging as a control (Figure 1). For cans lined with BPA epoxy, H_2S concentrations increased in all 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). For both BPA and BPA-NI liners, a significant increase in H_2S was observed for two of the white wines (W2 and W6) after only two months, and for all white and rosé wines by either four or eight months. For the two rosé wines and four of the six white wines, the highest H_2S concentration was observed at the final eight month time point. However, the two highest H_2S concentrations (43 µg/L in W2 and 53 µg/L in W6) were observed after four months of 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: for the BPA-epoxy-lined cans, the average relative standard deviation was 69% for cans stored for four months and 55% for cans stored for eight months. High can-to-can variation has been observed previously and has been credited to variation in liner thickness and heterogeneity in aluminum composition.

The same 10 commercial wines were also stored in their original glass packaging and analyzed after eight months of canning (Soares et al. 2019). Due to limited supplies, glass-packaged W6 was not available at eight months; however, H_2S had been measured in this wine after five 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 type (screwcap versus natural cork) in the unopened controls, indicating that this factor was unimportant in H_2S formation in the current experiment. H_2S concentrations after eight months storage in glass were significantly lower than the range observed in BPA-epoxy cans after eight months

	Red 1	Red 2	Rosé 1	Rosé 2	White 1	White 2	White 3	White 4	White 5	White 6
H₂S, epoxy-lined cans (µg/L)	0.4	0.3	1.4	7.4	8.0	39.7	2.3	14.3	18.3	35
H₂S, 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 Hydrogen sulfide (H_2S) as a function of storage time (one, two, four, or eight months) for 10 commercial wines packaged in replicate BPA-epoxy-lined cans (n = 3 per time point for each wine; error bars represent one standard deviation). Average H_2S levels after four and eight months for each wine stored in BPA-epoxy-lined cans or in glass are reported below the bar chart. n.d., no data.

(paired *t*-test, $p < 0.05$), which is in agreement with a recent survey of commercial wines in a separate report (Allison et al. 2022).

Full results for the cans lined with BPA-NI and acrylic are reported in Supplemental Figure 1. H₂S formation following eight months storage in cans lined with BPA-NI epoxy and BPA epoxy 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. (Supplemental Figure 2).

Wines in acrylic-lined cans rapidly formed suprathreshold concentrations of H₂S. After only one month of storage, median H₂S concentrations in acrylic cans (367 μg/L) were greater than the highest value (35 μg/L) reported in a survey of wines with "reductive" flaws (Siebert et al. 2010). The maximum H₂S production in acrylic-lined cans (1307 μg/L) was over 20-fold higher than that in cans lined with either BPA or BPA-NI epoxy, and formation across all wines was poorly correlated with production of H₂S for the same wines in BPA epoxy cans ($r^2 = 0.008$; Figure 2).

H₂S formation during long-term storage correlates with visible damage to the liner, but not with [Al]

Visible damage to the can liners was scored on a 0 to 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 Supplemental 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 of up to 2 mm), with no evidence of any material deposited on the surface. Blister appearance was similar to

that reported for blisters formed in beverage cans following exposure to high-alcohol hand sanitizers (Thomson and Bullied 2020). As with H₂S production, liner damage was not detected for most wines until after four months. The extent of damage to the BPA epoxy and BPA-NI epoxy can liners was well correlated with H₂S formation after eight months of storage (Spearman's test, $p < 0.05$; Figure 4).

Aluminum corrosion under acidic, anoxic conditions results in the oxidation of insoluble Al(0) to soluble Al(III) species and the concurrent formation of H₂ gas (Equation 2); thus, measurement of [Al] is proposed as a proxy for corrosion during beverage-can storage (Soares et al. 2019, Scrimgeour et al. 2020). To determine if the change in [Al] (Δ[Al]) and H₂S formation were correlated, [Al] was measured in the initial wines and at subsequent storage points in the canned wines. Initial concentrations of [Al] in the wines ranged from 0.5 to 2.1 mg/L, which is in agreement with a recent report (Karas et al. 2020). No significant increase in [Al] was

Figure 3 Representative images of cans scored with a "0" (top panel, undamaged BPA-epoxy) and "5" (bottom panel, badly damaged acrylic).
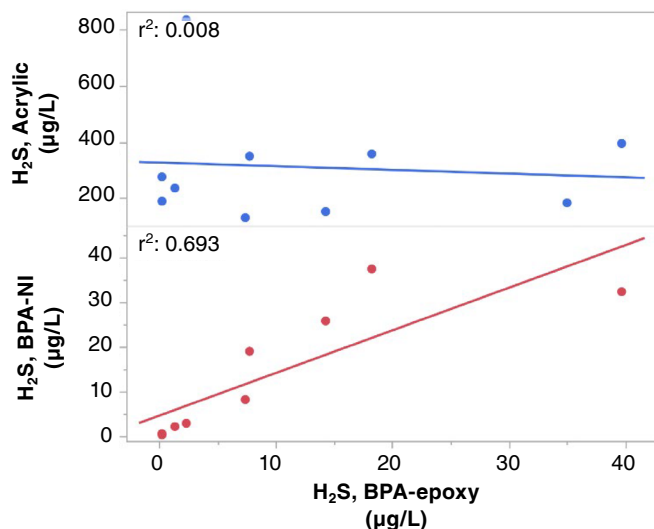
Figure 2 Linear regressions of hydrogen sulfide (H₂S) for wines stored in cans lined with BPA-epoxy versus acrylic (top panel) and BPA-epoxy versus BPA-NI (bottom panel). Each point represents an average H₂S value after four and eight months (n = 3 for each time point, n = 6 total).
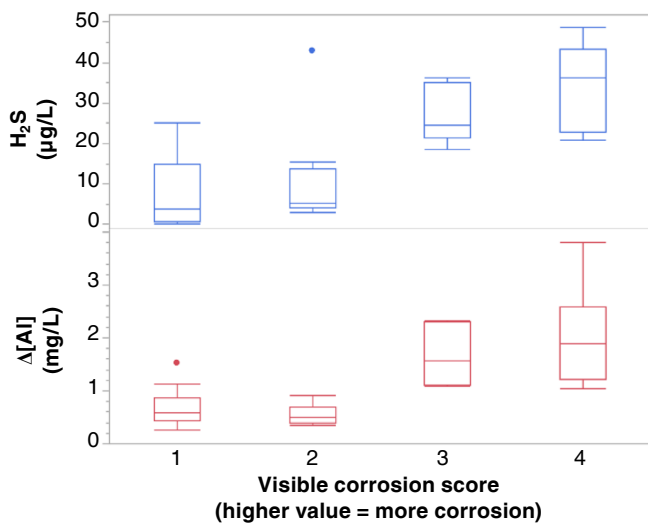
observed until four months. Concentrations increased with storage time after four months and reached a maximum after eight months for most wines. The highest Δ[Al] for the BPA epoxy liner was observed for W2 and was 2.29 mg/L after eight months, comparable to the increase in [Al] observed in a recent 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 eight months of storage (r^2 = 0.928; slope = 1.03; figure not shown). Like H₂S, Δ[Al] was much higher in acrylic-lined cans, in which Δ[Al] values as high as 4.49 mg/L were observed after two months. Because of the poor performance of the acrylic liners, no aluminum measurements were performed at four or eight months.

Only weak correlation was found between Δ[Al] and H₂S formation after one to eight months storage (r^2 = 0.189, Figure 5A). After eight months storage, the regression coefficient for Δ[Al] and H₂S was r^2 = 0.45 for epoxy-coated cans (designated by squares in Figure 5A). As a caveat, [Al] or H₂S could be lost from certain wines following their formation (e.g., Al (III) may form insoluble complexes with proteins) (Bengough and Harris 1954). Thus, these measurements may underestimate the extent of H₂S formation and aluminum oxidation during canned wine storage.

H₂S and Δ[Al] during long-term storage: Correlation with chemical composition
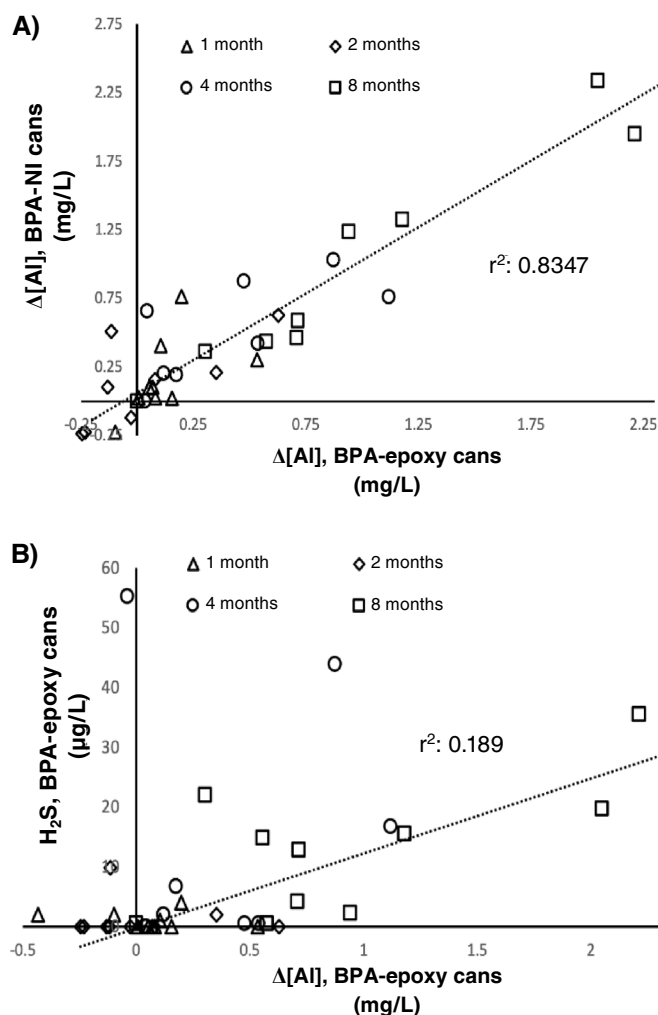
The compositions of the 10 wines under study were measured prior to canning (Table 1). Measurements included both common wine chemistry metrics (pH, TA, alcohol, residual sugar, free SO₂, total SO₂, and molecular SO₂) and components implicated in accelerating beverage can corrosion (Cu and Cl) (Coetzee 2021). The observed ranges for most compounds in this study were generally representa-

tive of the ranges reported in other surveys of commercial wines. For example, Cl 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 Cu. All wines in this study contained <0.1 mg/L Cu, with the exception of 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] versus [Average of H₂S at four months and eight months] were performed for each component. The average H₂S at four and eight months was used for regression analyses to account for variation in the timing of "peak" H₂S. The chemical parameters best correlated with H₂S formation were free SO₂, molecular SO₂, and pH, all with correlation coefficients of |r| > 0.8 (Figure 6A). A more modest correlation with H₂S pro-

Figure 4 Change in dissolved aluminum (Δ[Al]) and hydrogen sulfide (H₂S) for cans lined with BPA and BPA-NI epoxy and 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 H₂S were significantly correlated with visible damage (Spearman's rank order test; p < 0.001).

Figure 5 (**A**) Change in dissolved aluminum (Δ[Al]) in cans lined with BPA-NI epoxy versus BPA epoxy across all storage time points (one, two, four, and eight months) and wines. (**B**) Δ[Al] versus hydrogen sulfide (H₂S) (µg/L) for cans lined with BPA epoxy across all storage time points. Each point represents an average of three can replicates.

duction 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] versus Δ[Al] data after four and eight months. No significant correlation was observed at the four-month point for any component, but two components (pH, r = -0.59, and total SO_2, r = 0.61) were correlated with Δ[Al] after eight months.

Development of an accelerated-aging test for prediction of H₂S formation during long-term storage

We developed and validated 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. This approach was taken instead of performing accelerated aging on beverage cans to save on material costs and minimize space for storage of cans. It also allows faster throughput compared with 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 H₂S values, even with H₂S spiking experiments and omission of the coupon (data not shown). These poor results were determined to arise from variable and high levels of O_2, during either packaging or storage, presumably leading to oxidative losses of H₂S through one of several pathways (Kreitman et al. 2019). The challenge of maintaining low O_2 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 O_2 during preparation of wine samples for storage (Franco-Luesma and Ferreira 2016). 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 O_2 was limited by adding a small amount of LN_2 just prior to crimp capping the vials. With this approach, total package O_2 (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 acceptable precision for subsequent H₂S measurements following accelerated aging.

The silicone septa and PTFE/silicone septa allowed high levels of O_2 ingress during storage at elevated temperature (5.2 ± 0.4 mg/L and 3.2 ± 0.4 mg/L O_2, respectively, after seven days at 40°C;

Supplemental Figure 4), an observation that was unsurprising considering the high O_2 permeability of both Teflon and silicone. However, the butyl rubber and isoprene septa both allowed negligible amounts of O_2 ingress (<0.02 mg/L pickup after seven days at 40°C). Further testing with butyl rubber septa revealed that they allowed negligible O_2 ingress out to 14 days at 50°C (data not shown); thus, these were used for future accelerated-aging tests.

The use of coupons for corrosion testing is common in industrial settings, as it allows convenient and reproducible evaluations of metal-solution interactions (ASTM 2005). For the results in this work,
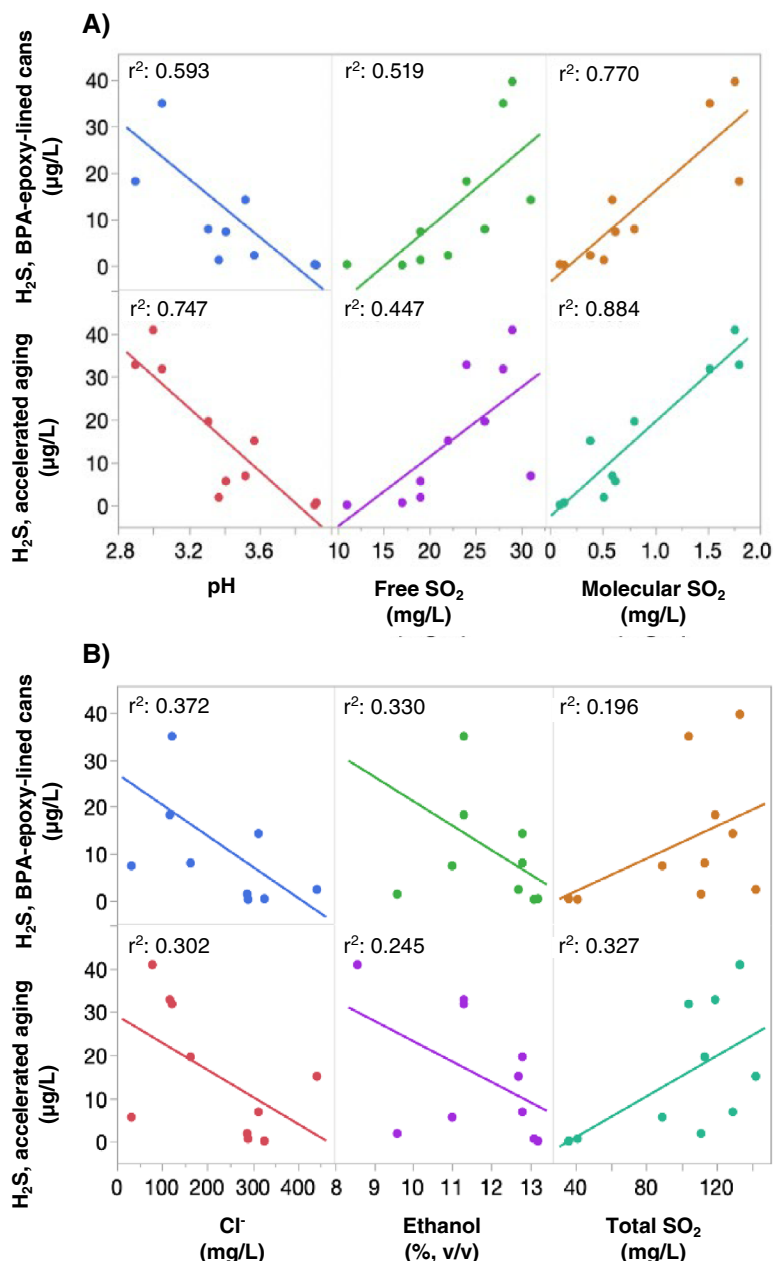
Figure 6 (**A**) Linear regressions of hydrogen sulfide (H₂S) formation and initial wine composition (pH, free SO_2, and molecular SO_2) following long-term storage in BPA-epoxy-lined cans (average of four and eight months) or under accelerated aging conditions with BPA-epoxy-lined coupons (average after three and 14 days at 50°C). (**B**) Linear regressions of H₂S formation and initial wine composition (chloride, ethanol, and total SO_2) following a long-term storage in BPA-epoxy-lined cans (average of four and eight months) or under accelerated aging conditions with BPA-epoxy-lined coupons (average after three and 14 days at 50°C).

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 bare aluminum to contact the wine and thus lead to high H_2S formation regardless of coupon coating. EVA was used to coat the edges of coupons to prevent the bare aluminum from interacting with the wine. To confirm that the EVA glue was inert, unlined aluminum coupons were prepared 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 versus 67 ± 4.3 µg/L for edge coating), indicating 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 contact between the wine and the coupon under accelerated conditions.

In preliminary experiments using two test wines, no detectable H_2S signal was observed at 40°C at three days, but H_2S could be detected at 50 and 60°C for the same period. However, at 60°C, the hot-melt glue was observed to soften and re-melt. Therefore, 50°C was selected for the validation experiments.

Accelerated aging with lined coupons predicts H_2S formation following long-term can storage, but accelerated aging with bare aluminum coupons does not

To determine an appropriate storage time for accelerated aging, wine and lined coupons (BPA epoxy, BPA-NI epoxy, and acrylic) were incubated at 50°C using the optimized conditions described above, and H_2S was measured. Control wines with no coupon ("glass storage") and wines

stored with bare aluminum coupons were also included. Storage experiments were performed for both three and 14 days, except for the BPA-NI epoxy coupons, for which only three days' storage was evaluated, due to limited coupon supply. Representative data for three wines (Red 1, Rosé 1, and White 2) are shown in Figure 7. As expected from results with long-term storage, the red wine produced negligible H_2S, and the lined coupons produced H_2S in the order acrylic > BPA-NI epoxy ~ BPA epoxy. Notably, negligible H_2S was formed in the glass-only control trials performed without coupons.

Across all wines, H_2S formed during long-term storage in BPA epoxy cans (average of the concentrations after four and eight months of storage) was well correlated with the average of three and 14 days of accelerated aging with BPA-epoxy-lined coupons (r^2 = 0.793; Figure 8). Acceptable correlation was also observed when using only three- or 14-day results (r^2 > 0.65, Supplemental Figure 5). The range of H_2S formed after 14 days of accelerated aging (0 to 56 µg/L) was comparable to the range observed after eight months, despite requiring ~17-fold less time. As with long-term aging, H_2S formation with epoxy-lined coupons was best correlated with molecular SO_2 (r^2 = 0.884, Figure 6A).

H_2S formation during long-term aging and three-day accelerated aging conditions was also correlated for BPA-NI epoxy lined cans and coupons (r^2 =0.65; Supplemental Figure 4, top) but was poorly correlated for acrylic coupons and cans (r^2 = 0.051; Supplemental 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 three days (Figure 8). H_2S production was uncorrelated for bare aluminum coupons under accelerated conditions and BPA-epoxy-coated cans during long-term storage conditions (r^2 < 0.15; Figure 8).

Validation of the 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 ethanol levels (8, 13, and 18%), pH (2.75 to 4), and free SO_2 (20 to 80 mg/L), with W3 used as a base (the white wine that produced the least H_2S following long-term storage). These values resulted in molecular SO_2 ranging from 0.5 to 8.4 mg/L at 20°C, or 2.06 to 25 mg/L at 50°C (the temperature of the accelerated-aging test). Wine samples were subjected to accelerated aging with coupons lined with BPA epoxy, and H_2S was 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), as indicated by the fact that 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.
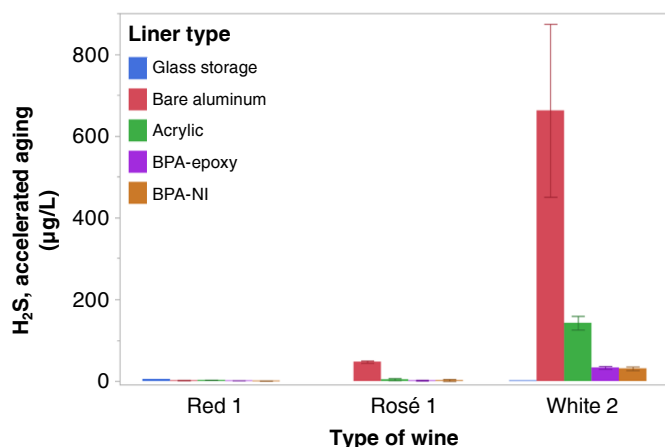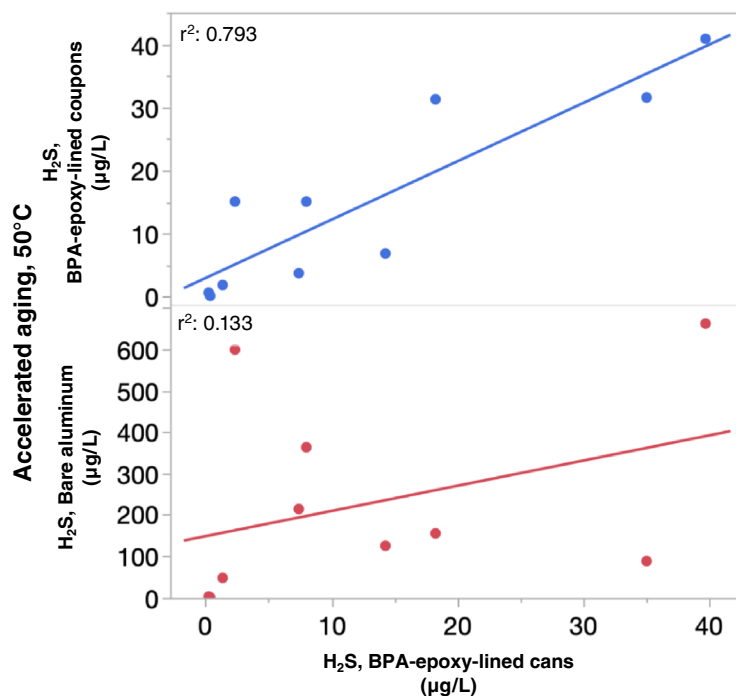
Figure 7 Hydrogen sulfide (H_2S) formation under accelerated aging conditions (three days, 50°C) for representative red, rosé, and white wines using either no coupon (glass control), bare aluminum coupons, acrylic-lined coupons, BPA-epoxy-lined coupons, or BPA-NI-epoxy-lined coupons. Three replicates were run per trial, and error bars represent one standard error.

Discussion

Classic research 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 and trade journal articles report that wines packaged in aluminum beverage cans will develop more H_2S during storage (Stokes and Barics 2013, Scrimgeour et al. 2019). 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 versus glass-packaged conditions has not been reported in the peer-reviewed literature, despite Rankine's proposal of Equation 1 in 1983 (Rankine 1983).

In this work, multiple commercial wines were stored either in 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, Supplemental Figure 1) after only two months and would not be acceptable for commercial use. In cans lined with BPA or BPA-NI epoxy, some white wines developed H_2S levels greater than 10 µg/L after four months of storage at room temperature (Figure 1) and, in some cases, after 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 levels showed that increasing molecular SO_2 yielded a good correlation with H_2S formation, whereas increasing free SO_2 or pH alone were less predictive (Figure 9). However, because molecular SO_2 is proportional to [free SO_2] × [H^+], it is unclear whether the observed increase in H_2S is due to molecular SO_2 or to 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 hypothesized by others (Rankine 1983, Stokes and Barics 2013). 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, and W6), which should allow low O_2 ingress compared to cans (Thompson-Witrick et al. 2021). Furthermore, this alternative "precursor-release" hypothesis would

Figure 8 Linear regressions of hydrogen sulfide (H_2S) formation during long-term storage in BPA-epoxy-lined cans (average of four and eight months) versus either accelerated aging in the presence of BPA-epoxy-lined coupons (top panel) or bare aluminum coupons (bottom panel).
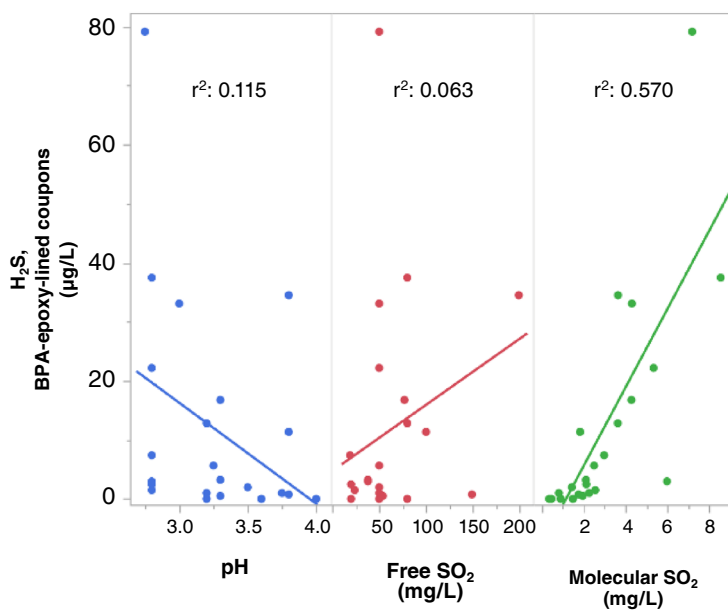
Figure 9 Linear regressions of hydrogen sulfide (H_2S) formation in model wine solutions as a function of molecular SO_2 (calculated at 20°C), pH, and free SO_2 for spiked wines stored under accelerated aging conditions (three days at 50°C with BPA-epoxy-coated coupons).

not explain why accelerated aging of wines in the absence of coupons result in negligible H$_2$S formation (Figure 7).

Based on the hypothesis that molecular SO$_2$ (or free SO$_2$ × pH) is the cause of H$_2$S 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. (2022), Siebert et al. (2010), and references therein, the odor detection threshold of H$_2$S is ~1 µg/L, but the recognition threshold is possibly as high as 30 µg/L. Using an intermediate target of maintaining H$_2$S 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 six months and room temperature storage, and this limit would need to be decreased if longer shelf lives were desired or higher storage temperatures were expected.

The lowest levels of H$_2$S formation were 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. This and related techniques overestimate molecular and free SO$_2$ by a factor of three, on average, due to the artifactual measurement of weakly bound anthocyanin-bisulfite complexes. 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, thus red wines are expected to be of relatively low concern for H$_2$S formation during can storage. Alternatively, the low H$_2$S levels in the canned red wines could result from direct effects of polyphenols in these wines on H$_2$S 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 two reasons:

If H$_2$S formation depended only on the initial presence of pores, then H$_2$S formation with lined and bare coupons should be well correlated across wines, albeit with slower H$_2$S production for lined coupons. This hypothesis was explicitly tested by comparing H$_2$S 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).

Furthermore, significant increases in H$_2$S are detected in some wines by two months, and in most wines by four months (Figure 1). Significant increases in [Al] (Δ[Al]), however, are typically not seen until eight months (Figure 5). This suggests that reactions that allow H$_2$S formation occur before the corrosion reactions responsible for aluminum dissolution.

An alternative hypothesis to the initial presence of liner pores is that SO$_2$ induces liner failure and H$_2$S formation. SO$_2$ gas has been reported to degrade polyester coatings in steel, which the authors suggested could be due to the reductive nature of the compound (Ozcan et al. 2002). In the current work, the best predictor of H$_2$S formation and liner degradation is molecular SO$_2$. In principle, this neutral, volatile form could diffuse through liner coatings as it does through certain polymeric membranes; however, there are no published studies on diffusion rates of SO$_2$ through the liner materials used in the current study. A complimentary possibility is that the combination of free SO$_2$ and low pH (which manifests as high molecular SO$_2$) is responsible for initial liner degradation, after which molecular SO$_2$ is better able to reach and react with the aluminum metal. Initial liner damage would also allow H$^+$ to reach the metal surface and form H$_2$ gas, which may further damage the liner through blistering (Vargel 2004). Of these two, the second hypothesis seems better supported by the data, considering the sharp increase in H$_2$S after four or eight months in several wines, which is more compatible with liner failure than with continuous SO$_2$ diffusion. The correlation of visible liner damage with Δ[Al] (Figure 4) also supports the conclusion that initial liner damage by SO$_2$ allows further corrosive events.

In either case, once the liner is sufficiently damaged, the bulk wine will be able to contact the metal surface, and corrosion occurs under acidic, anoxic conditions to generate [Al(III)] and H$_2$ (Equation 2). [Al(III)] will also be formed by reaction of Al^0 and SO$_2$, but this will be less important quantitatively; based on stoichiometry and H$_2$S evolution, <100 µg/L [Al] will be generated via SO$_2$ for epoxy-lined cans, or <10% of the observed Δ[Al]. In support of this, pH is better correlated with Δ[Al] than with molecular and free SO$_2$, and lower pH has been reported elsewhere to increase corrosion in beverage cans (Seruga et al. 1994, Stokes and Barics 2013, Crouchiere 2020).

The low correlation of Cl and Cu with both H$_2$S formation or Δ[Al] was somewhat surprising, as both components are well known to increase corrosion (Vargel 2004), and can manufacturers generally provide limits for both components. Cl, for example, is well known to exacerbate aluminum pitting corrosion through formation of AlCl$_4^-$ at the anode (Natishan et al. 2014). However, many of these studies use Cl levels comparable to those found in salt water at the g/L scale (Natishan and O'Grady 2014), exceeding values we observed (<500 mg/L) in wines. Similarly, Cu is reported to facilitate cathodic reactions and corrosion and could also act as a source of H$_2$S through copper-sulfhydryl precursors. The lack of correlation may be in part because of the limited number of wines in this study with high levels of Cu. Spiking studies to evaluate the effects of Cu on canned wine stability would be interesting, with the caveats that Cu salts added to wines are initially more reactive ("labile") and that they lose reactivity through complexation with sulfhydryls following storage (Clark et al. 2016).

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

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 useful for rapidly testing the suitability of a wine for canning and long-term storage for up to eight months at room temperature, at least for the epoxy-based liners (BPA epoxy and BPA-NI). H_2S formation at cooler storage temperatures (e.g., 4°C) 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 aluminum beverage cans lined with BPA or BPA-NI epoxy will produce suprathreshold concentrations of H_2S within eight months, and, in some cases, in as little as two months. Very high production of H_2S is observed within one month for acrylic-lined cans. H_2S production during long-term storage correlates well with visible liner degradation but not with increased $[Al]$. Results from accelerated aging with spiked wine samples support the hypotheses that H_2S can be formed from reaction of SO_2 with aluminum (Equation 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 four to eight months of 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 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 and kombucha) and thus has the potential to increase the effective use of beverage cans as a sustainable option for single-use packaging.

Acknowledgments

Supplemental Data

The following supplemental materials are available for this article at ajevonline.org:

Supplemental Figure 1 Hydrogen sulfide (H_2S) produced after one, two, four, and eight months storage in cans coated with BPA-NI (top panel) or acrylic (bottom panel).

Supplemental Figure 2 Total oxygen ingress during storage of water in crimp-capped vials at 40°C for seven days, as a function of septum material. PTFE: polytetrafluoroethylene.

Supplemental Figure 3 Regression plots of hydrogen sulfide (H_2S) formed under accelerated aging conditions (three, 14, or average of three and 14 days) versus H_2S formed during long-term aging (four, eight, or average of four and eight months). Accelerated-aging conditions used coupons lined with BPA epoxy at 50°C, and long-term aging used cans lined with BPA epoxy. Each point represents one commercial wine, prepared in triplicate.

Supplemental Figure 4 Regression plots of hydrogen sulfide (H_2S) formed under three days of accelerated-aging conditions versus H_2S formed during long-term aging (four, eight, or an average of four and eight months). Cans and coupons were lined with BPA-NI epoxy (top panel) or acrylic (bottom panel). Each point represents a commercial wine prepared in triplicate.

Supplemental Figure 5 Corrosion scores for commercial wines stored in cans lined with BPA-epoxy and BPA-NI epoxy after eight months of storage. For each wine, n = 3 or n = 6, depending on the availability of cans.

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