Canned wine
Looking for a silver lining

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While wine packaged in cans is a fast-growing segment of the global market with strong consumer appeal, some canned wines have been affected by 'reductive' characters. A comprehensive series of studies investigated the reasons behind this phenomenon and explored a range of mitigation options to ensure the ongoing success and growth of wine in this packaging format is supported.

IN BRIEF

- **Packaging wine in cans provides a range of benefits including convenience, value and appeal to younger consumers.**
- **Some wines packaged in cans have been affected by 'reductive' characters, predominantly caused by hydrogen sulfide (H_2S), shortening the effective shelf life and posing a risk to the ongoing success of this packaging format.**
- **A series of trials were conducted to understand the importance of individual wine attributes in determining the risk of H_2S formation in canned wine.**
- **High concentrations of copper and chloride can lead to increased aluminium concentration and this accelerates the formation of H_2S.**
- **Use of a PVI/PVP co-polymer to remove copper and decrease the risk of aluminium migration from the can into the wine was found to be effective in delaying the onset of H_2S production in canned wines.**
- **Selecting wines that have lower risk factors for H_2S formation is also important in minimising the risk of H_2S formation and extending shelf life.**

INTRODUCTION

Canned wine is one of the fastest growing segments in global wine consumption, with the current global market estimated to be worth AUD$130 million and worldwide sales predicted to grow with a compound annual growth rate of 5-10% over the next five years (Research and markets report 2022) Consumer interest in this category, especially with millennials, continues to thrive due to factors including value for money, packaging design, convenience and perceived sustainability.

The current size of the Australian domestic market for canned wine is approximately $12 million in annual sales, with the growth in canned wine (at 12% per annum) outperforming bottled wine, which has relatively flat growth at 0.4% (IRI report 2022). The growth of canned wine has slowed in recent years in Australia, partly due to increasing competition in the category from hard seltzers and other RTD products.

During the last few years, it has become very clear that some wines packaged in cans are particularly susceptible to the formation of 'reductive' characters within three to six months of packaging, with the main culprit being hydrogen sulfide (H_2S), which can impart a 'rotten egg' aroma (Allison *et al.* 2020). This can result in wines being rejected by the consumer and products being recalled from the market, so it is an issue that poses a significant risk to the reputation of Australian wine.

SHELF-LIFE ISSUES DRIVE NEED FOR COMMERCIAL STUDY

Aluminium beverage cans contain a protective barrier film that is applied to the inner surface of the can body and lid. This is typically a water-based epoxy coating, designed to keep the product from being in contact with the aluminium can surface. Compared with other beverages, such as beer and soft drinks, wine is a relatively aggressive matrix due to its low pH and the presence of sulfur dioxide (SO_2). This means that a thicker barrier film is typically applied to cans that are destined to be filled with wines.

The extent of the shelf-life issues experienced by commercial canned wine products, however, made it clear that a better understanding of the chemical pathways involved in H_2S formation in this format was required. With this in mind, the AWRI set up a commercial study to investigate the true extent of the problem in canned wines, identifying the key risk factors and to develop practical industry solutions. The study included a consortium of wine producers and suppliers, based both in Australia and the USA.

A detailed series of trials were carefully designed to understand the importance of individual wine attributes on product shelf life and how these factors could be better controlled to mitigate the risk of H_2S formation. Consortium members were asked to supply existing examples of commercial canned wines, as well as those that were earmarked for future release in this format, in order to understand the real-world impact.

BENCHMARKING OF COMMERCIAL CANNED WINES

Samples of 16 commercial canned wine products were monitored over a five-month period for concentrations of aluminium, free and total SO_2 and H_2S. The free SO_2 concentrations in the wines were fairly typical for wine products that had been packaged within a six-month period (minimum 9mg/L, maximum 29mg/L, average 17mg/L).

Most of the wines experienced a significant increase in aluminium concentration post-packaging (Figure 1), despite the presence of the protective barrier film on the internal surface. This is not a problem that is unique to wine products; benchmarking of other canned beverages indicated that aluminium concentration increases can occur in other drinks, such as cider and kombucha.

Australian wines typically contain, on average, around 300µg/L and 700µg/L aluminium for red and white wines respectively (Wilkes 2018). Despite the increases in aluminium concentration seen in canned wine products during this study, none of the wines exhibited aluminium levels anywhere near the international limit of 8000µg/L, with concentrations well below levels considered to have negative health implications.

Scanning electron microscopy and subsequent x-ray analysis of sections taken from the body and lids of significantly affected commercial canned wines indicated evidence of pitting on the inner surfaces, providing a pathway for the migration of aluminium into the wine (Figure 2).

A review of the corrosion chemistry of aluminium indicated that the pH, copper and chloride concentration in certain media could lead to pitting in aluminium (oxide) surfaces. It is presumed that this corrosion chemistry is a driving force in the increases in aluminium concentration seen in commercial canned wines, despite the presence of the supposedly protective barrier film on the inner surface of the cans.

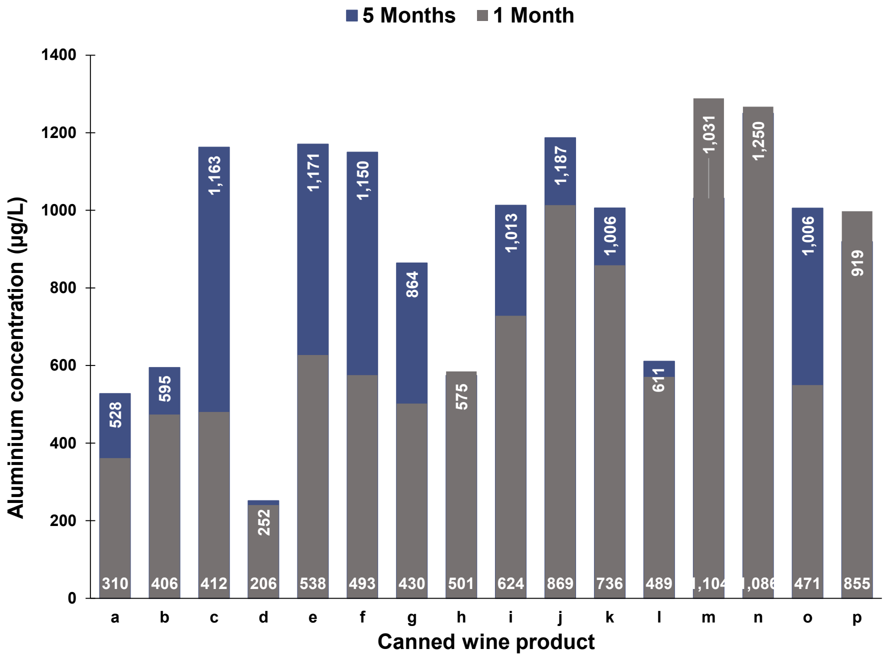

Figure 1. Aluminium concentrations in 16 commercially canned wine products, one and five months post-packaging.

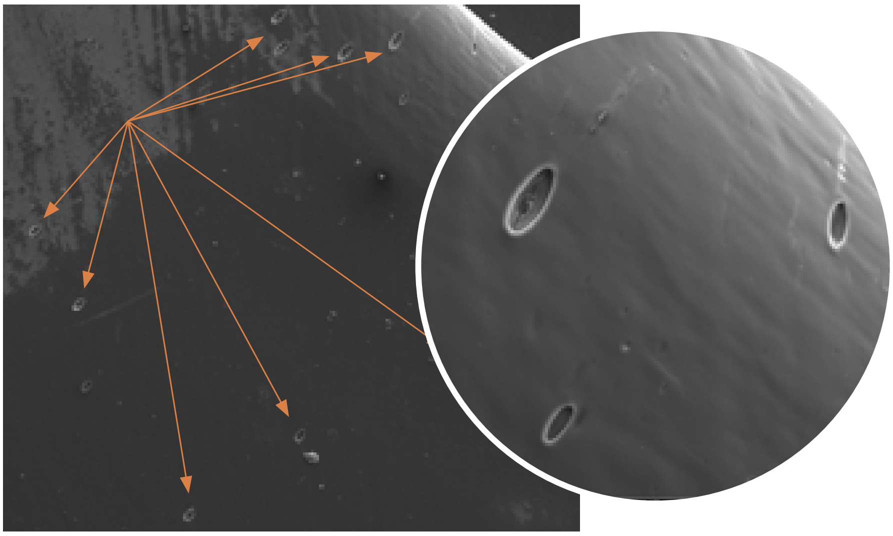

Figure 2. Evidence of pitting on the inner surface of the can lid for a commercial wine product: (left) low magnification image, showing multiple pitting sites; (right) high magnification image, showing close-up of pitting sites.

Aluminium in its elemental form (i.e. oxidation state of zero) is known to react with SO_2 to form H_2S. This provides a chemical pathway for H_2S formation that does not exist in wines packaged in glass bottles. Trials at the AWRI have shown that aluminium ions (i.e. in salt form) do not contribute to the development of 'reductive' compounds, confirming the importance of the wine/aluminium metal interaction.

The canned commercial wines showed significant variation in the concentration of H_2S over the five-month period (Figure 3), with some exhibiting levels significantly higher than the nominal aroma perception threshold (1.1-1.6µg/L). An informal sensory assessment of these commercial wines was also carried out after five months, with a number of the products exhibiting 'rotten egg', 'sulfurous', 'vegetal', 'rubbery', 'garlic' and 'onion' aromas, depending on the wine product matrix.

The potential impact of increased aluminium concentration on the quality of canned commercial wines was, unfortunately, difficult to predict. This was due to variations in can filling practices, variable headspace volume (ullage) in canning production runs and differences in wine attributes. It is also difficult to predict the potential release of free H_2S in commercial wines during storage (irrespective of the packaging type), resulting in no direct correlation between aluminium concentration and H_2S concentration.

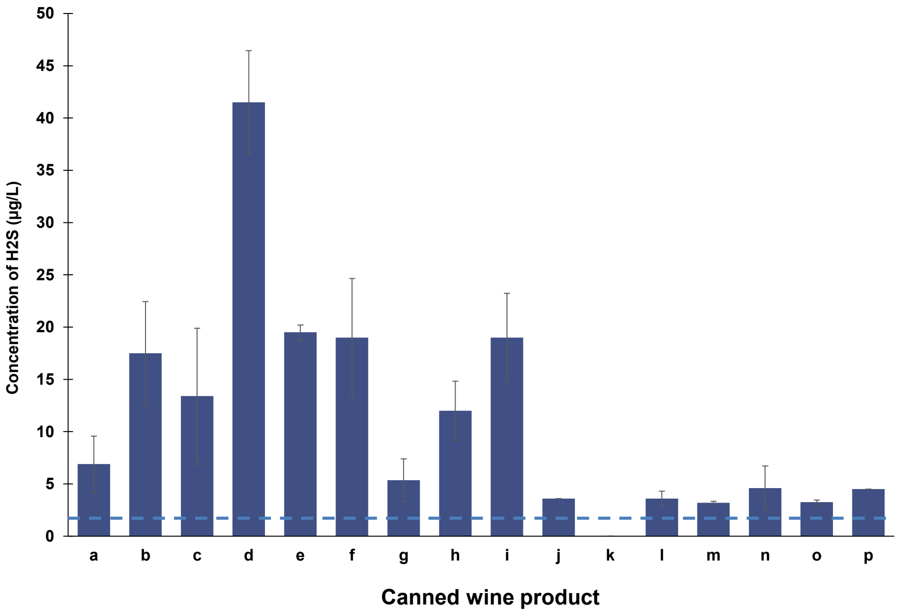

Figure 3. Concentration of H_2S in 16 different commercial canned wine products (a to p) after five months. The aroma perception threshold range for H_2S is 1.1-1.6µg/L (shown as a dotted line).

UNDERSTANDING THE DEVELOPMENT OF 'REDUCTIVE' COMPOUNDS

In order to better understand the role of the individual wine attributes in the development of H_2S in canned wines, a series of bench-scale experiments were set up in glass ampoules, using commercially-available wines and elevated temperatures to accelerate the resulting reactions. These experiments showed that:

- high copper concentration (>0.2mg/L) can lead to significant aluminium increases and speed up the formation of H_2S, especially in a low oxygen concentration environment
- the presence of chloride at relatively high concentrations (>100mg/L) can increase aluminium concentration and, consequently, H_2S concentration
- the presence of aluminium (metal) accelerates the formation of H_2S levels
- the onset of H_2S formation can be delayed if the copper concentration is significantly decreased, even when aluminium (metal) is present
- the impact of aluminium on H_2S formation is lower when pH is higher and SO_2 concentration is lower.

ASSESSING THE EFFECTIVENESS OF MITIGATION STRATEGIES FOR DECREASING H_2S FORMATION

Based on this, a mitigation strategy targeting the removal of copper from the wine prior to canning was formulated. Through a series of bench-top trials, the most effective method identified involved the use of cross-linked (poly-vinyl imidazole/poly-vinylpyrrolidone [PVI/PVP]) co-polymers to scavenge the copper species. These types of polymers are commonly used for the removal of heavy metals from wastewater and were approved for use as processing aids in Australian wine production in 2018.

Trials to assess these products involved the addition of co-polymers to wine samples at the supplier-recommended dose rates, with nitrogen gas used to purge the treatment vessel, both before and after filling. Samples were stirred for three hours before removal of the co-polymers using a 0.2µm regenerated cellulose filter. Analysis was carried out using inductively coupled plasma mass spectrometry to determine the concentration of various metals in treated and untreated samples.

A detailed benchmarking trial incorporating a series of 38 commercial wines (19 red and 19 white wines) treated with two commercially-available PVI/PVP co-polymers highlighted the impact of the treatment on copper concentration. Copper concentration decreases were in the order of ~60% and ~30% for white and red wines, respectively (Figure 4, see page 33). Both products showed high selectivity for divalent and trivalent metals (such as Fe^{2+} and Fe^{3+}) in both wine types, including naturally-occurring levels of aluminium.

The treatment of wines with PVI/PVP co-polymers was shown to decrease the risk of the corrosion process occurring at the aluminium (oxide) surface and subsequent migration of aluminium into the wine after canning. To date, this appears to be the most effective method for delaying the onset of H_2S production in most canned wines. This appears to be a particularly effective treatment as some of the copper removed is often bound to naturally-occurring sulfides, and its removal therefore decreases the residual pool of sulfides in the wine and the potential risk of their release at a later time.

EVALUATING THE IMPACT OF TREATMENT STRATEGIES ON CANNED WINE SHELF LIFE

A series of nine commercial wines provided by the consortium members were screened, treated with PVI/PVP and packaged using the AWRI's small-scale packaging facility. Chemical and sensory analyses were then carried out over a six-month period for the candidate wines (both treated and untreated). A sub-set of three of these wines was also packaged into cans with an alternate barrier film for comparative purposes.

This trial showed that the risk of reductive characters in canned wines can be minimised if wines with a low risk profile are pre-selected according to the known risk factors. This can be combined with treatment using a commercial cross-linked polymer prior to canning to decrease the risk of aluminium migration into the wines and the subsequent formation of H_2S.

In general, the treated wines showed lower increases in aluminium and H_2S during the six months after canning (Figure 5a) (Figure 5b, see page 34). Overall, resulting H_2S concentrations were lower than seen in previous benchmarking studies on canned wines.

Sensory evaluation of these wines was carried out using the AWRI's technical quality panel who assessed colour, aroma, flavour and evidence of any taint/fault. Each pair of wines (control vs treated) was assessed using a compare-and-contrast method. This evaluation showed comparable quality ratings for the control and treated wines, with no obvious taints or faults attributed to the PVI/PVP treatment process (Figure 6, see page 34).

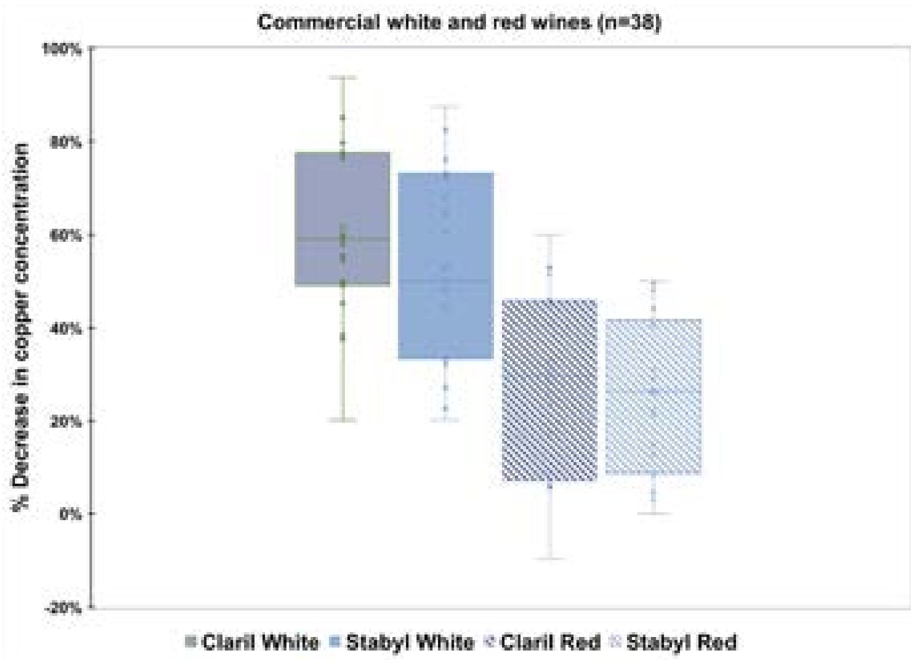

Figure 4. Percentage decreases of copper concentration observed in white wine treated with four PVI/PVP cross-linked polymer products, relative to the original base wine concentration. Individual results for each wine are indicated by circles, and the mean result is shown by the X in each box. The boxes represent the spread from the first quartile to the third quartile of the data, with the horizontal line within the box representing the median value. The 'whisker' lines above and/or below each box extend as far as the minimum and maximum values measured, excluding outliers.

FUTURE WORK

This body of work has highlighted that wine products are notoriously challenging to package into cans. Using cans with a thicker barrier film weight will decrease the risk of aluminium migration and subsequent formation of H_2S, but it does not resolve the problem for all wines. Careful pre-selection of wines so that the risks from copper and chloride concentration, pH and SO_2 levels are low, can decrease some of the risk of negative sensory outcomes with canned wines. When combined with the use of cross-linked polymers (to remove copper and any bound sulfides) these approaches have been shown to be effective tools in extending the shelf-life of canned wines.

During this study, a parallel body of work commenced to develop a simple laboratory test that can be used to assess the potential impact of different wines on aluminium migration from the inner can surface, and therefore predict likely issues with H_2S formation. This involves the creation of aluminium coupons from the inner can surface and coating them with an inert polymer-based film prior to immersion in a test wine matrix at elevated temperature. Once this method has

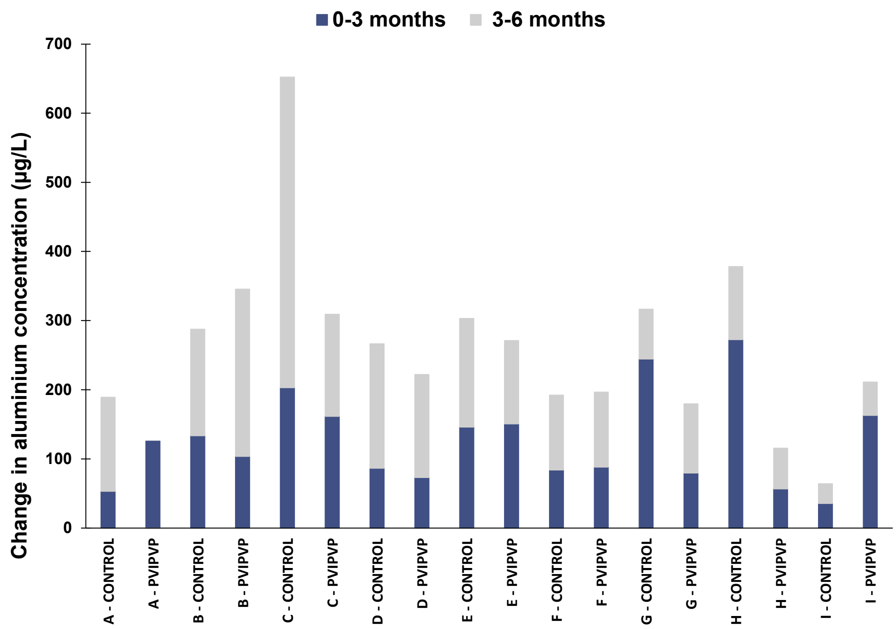

Figure 5a. Changes in aluminium concentration relative to the concentration at the time of canning in control and PVI/PVP-treated wines over 0-3 months and 3-6 months from canning.

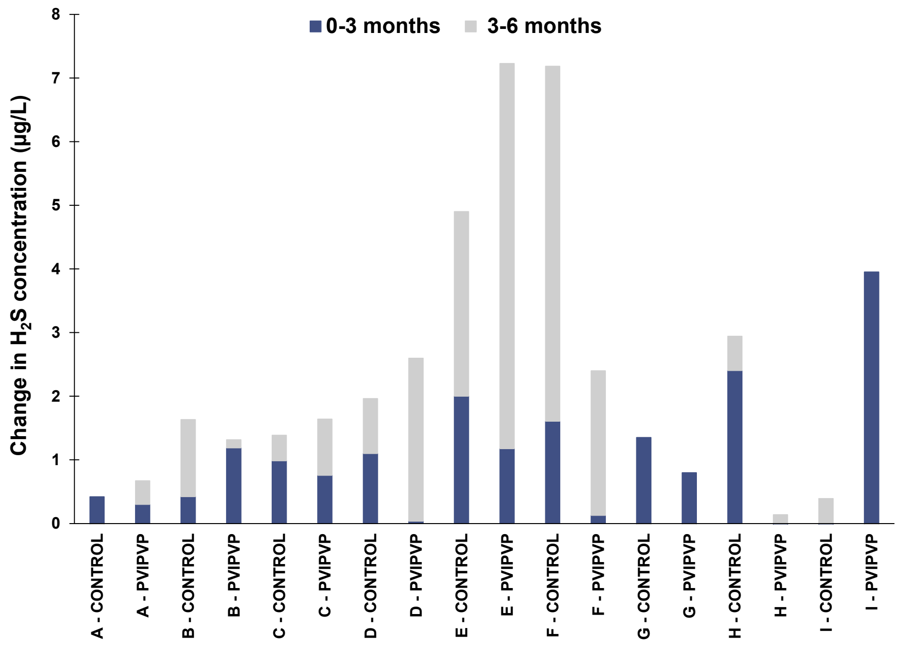

Figure 5b. Changes in H_2S concentration relative to the concentration at the time of canning in control and PVI/PVP-treated wines over 0-3 months and 3-6 months from canning.

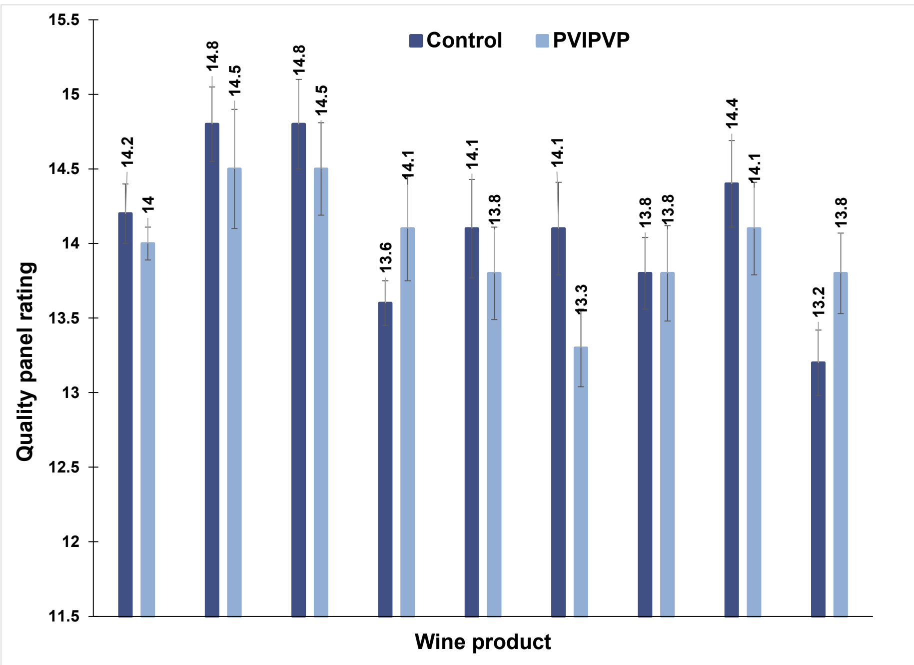

Figure 6. Quality panel ratings for nine commercial wines, each with control (untreated) and PVI/PVP-treated samples. Bars show average ratings awarded across ten panellists, with the standard error indicated by error bars.

been properly established, it will be validated prior to being made available commercially.

The outcomes from the consortium study will shortly be published in a technical guideline document for industry practitioners. A high level summary is already available through the Wine Packaging Guideline document issued by Australian Grape and Wine Inc. (September 2022). Some of the recommendations delivered by this body of work have also been incorporated into the handbook 'The Winemaker's Guide to Wine in a Can' (WineTech 2021).

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