Measuring stinky ferments *in situ*

In this second of two articles on tank instrumentation, AWRI Senior Engineer **Simon Nordestgaard** reports on some experiences using hydrogen sulfide and oxidation-reduction potential (ORP) sensors to monitor winery fermentations.

Figure 1. Electrochemical hydrogen sulfide sensor (~20 mm diameter).

Introduction

Winemakers regularly smell samples from ferments for signs of hydrogen sulfide. If detected, ferments might be aerated or given additions of nutrients or copper. Ideally, hydrogen sulfide (or conditions likely to lead to its formation) would be measured in-tank and remediation automated. Headspace hydrogen sulfide sensors and liquid oxidation-reduction potential (ORP) probes are two plausible measurement approaches that could facilitate this.

Headspace hydrogen sulfide sensors

Electrochemical hydrogen sulfide sensors (e.g. Figure 1) are commonly used in air quality monitoring. The sensors are small and easily incorporated into portable safety equipment. They are also relatively cheap, costing <$100 (although necessary electronics, housings, sampling valves and pumps, etc. can add significantly to the final system cost).

A commercially available system for monitoring wine fermentations that incorporated this style of sensor was trialled by the AWRI (Figure 2). The system has a pump and series of valves that allow it to draw gas intermittently from the headspace of up to five fermenters into a sensing chamber. The tubing for drawing the sample from the headspace is fitted inside the turret of the tank (Figure 3). For each fermenter, the system is purged with fresh air for four minutes, then purged with the headspace gas from the fermenter for two minutes before the measurement is made. The sequence is then repeated for the other

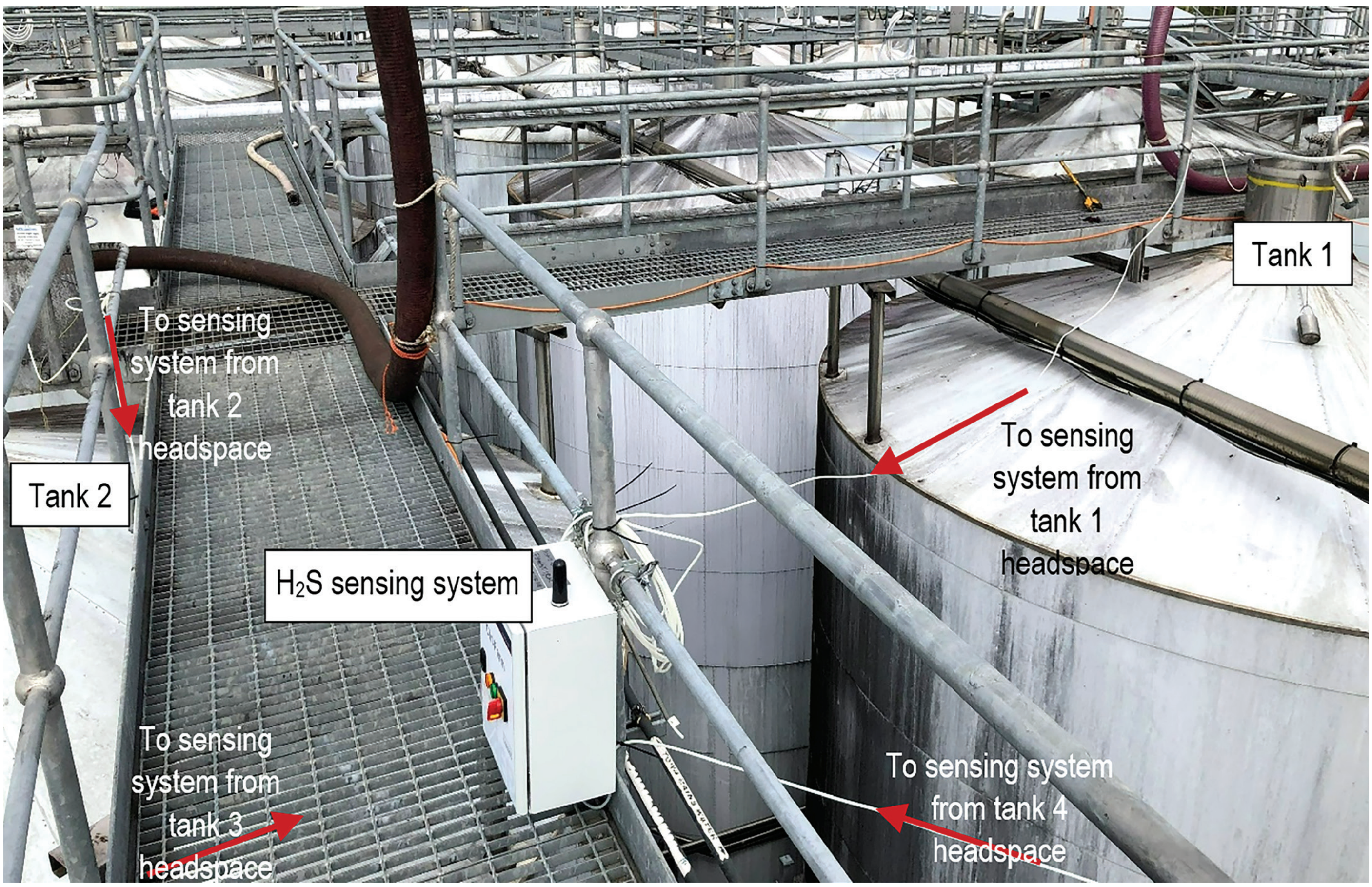

Figure 2. Layout for the hydrogen sulfide (H_2S) sensing system at a winery in 2019 (four red fermenters being measured).

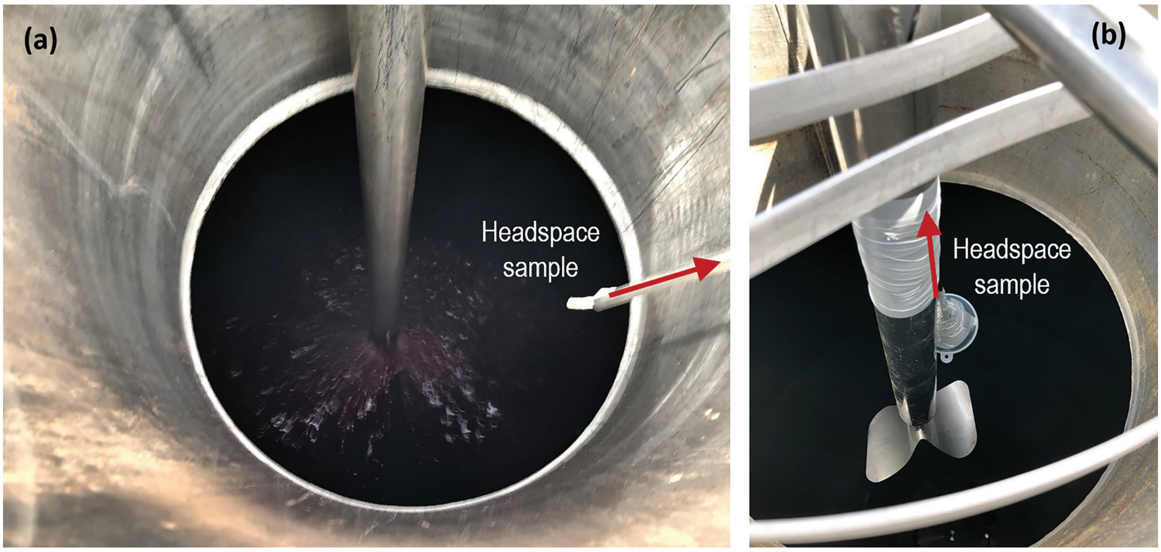

Figure 3. Headspace sampling from red fermenters: (a) 2019 configuration with tube running inside a thin metal tube hooked over tank lip, and (b) 2020 configuration with tube taped to irrigator pipe (with an upside-down funnel on the tube to try and prevent drips around the tube inlet being drawn into the system).

fermenters. Data from the system is sent intermittently to a cloud platform via an integrated 4G modem, allowing remote monitoring.

2019 vintage – Initial successes but daily fluctuations in measurements

Hydrogen sulfide was measured in four fermenters in 2019 (i.e. four of the five sensing channels were used for fermenters, with the fifth channel being used as an air control). The typical ferment size was 150 t and 15 ferments were monitored in total. The first ferment tested (Figure 4a) was in a tank that was sparged constantly with compressed air by the winemaker in an effort to prevent H_2S formation. However, the ferment displayed H_2S characters towards the end of ferment and required a copper treatment. It was later discovered that the sparger had blocked just prior to the elevation in H_2S levels. These observations leant anecdotal support to the merit of the system being trialled. However, as the vintage progressed, the results were often less clear. Ferments that were ultimately treated with larger amounts of diammonium phosphate or needed a copper addition tended to show slightly higher H_2S levels, but the results were hidden within daily fluctuations. The measured H_2S value would inexplicably drop to zero for periods each day. Most commonly this happened during the middle of the day, and the effect was not clearly correlated with temperature or the timing of pump-overs or additions.

After the 2019 vintage, the system was dismantled. Some red residues were found on the sensor and in the adjacent tubing. Evidently at least once during vintage some fermenting juice was drawn into the system, despite the installation position of the headspace sampling tube being always above the liquid level. A new sensor was sourced and the fouled sensor was replaced. It was decided to use an inverted cone in any later trials

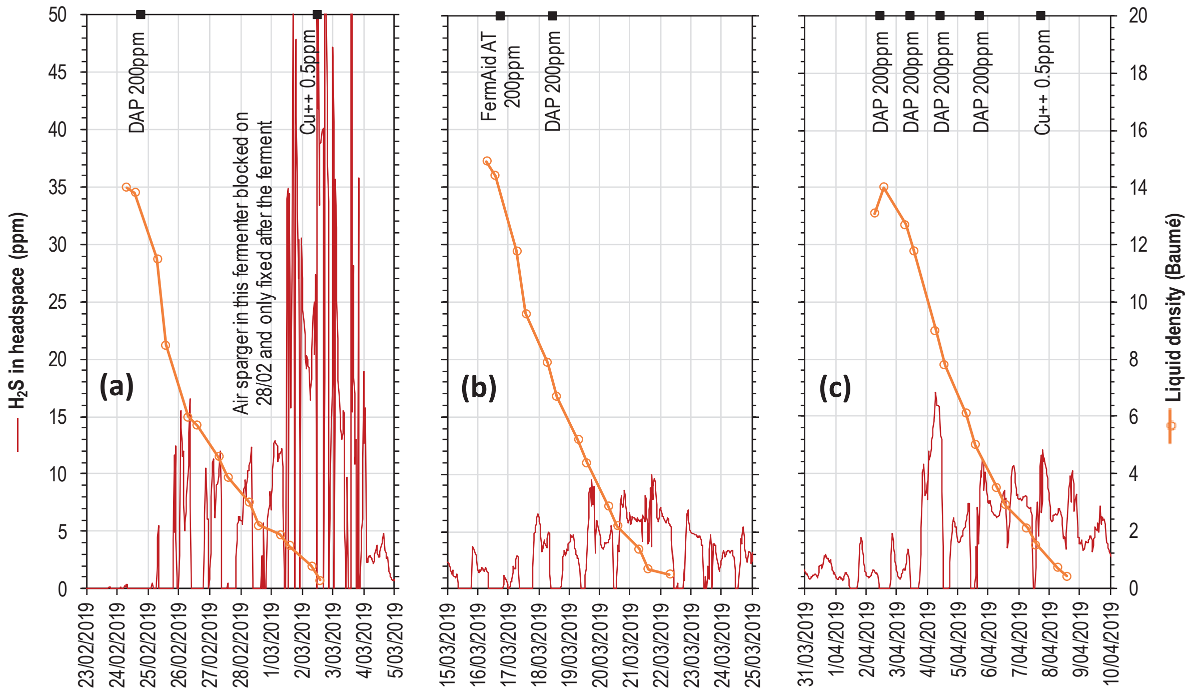

Figure 4. Hydrogen sulfide measured during 3 of 15 red ferments monitored during vintage 2019: (a) 162 t of Shiraz, (b) 132 t of Cabernet Sauvignon, (c) 151 t of Cabernet Sauvignon (approximate timings of nutrient and copper additions are marked).

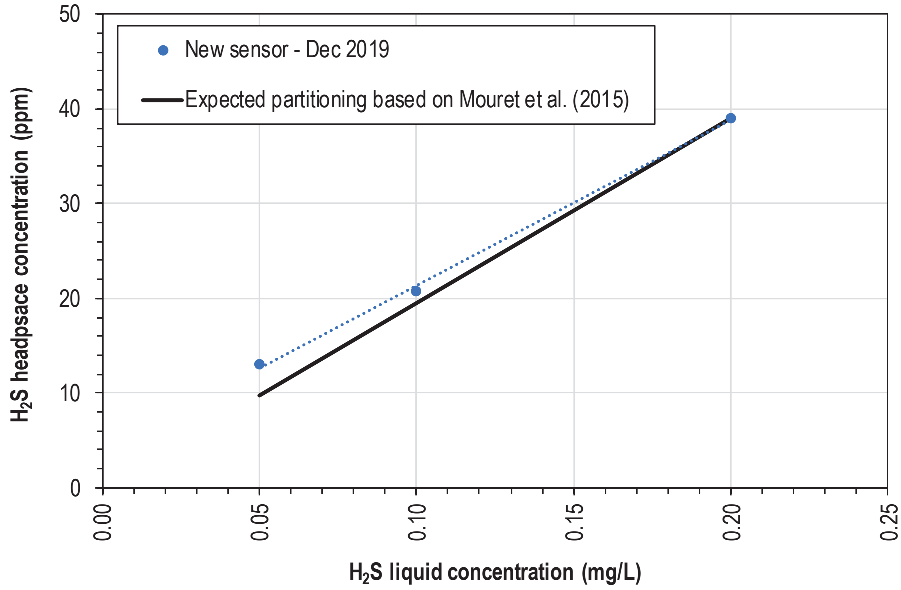

Figure 5. Relationship between H_2S liquid concentration and headspace concentration of H_2S measured using the H_2S sensing system in laboratory experiments.

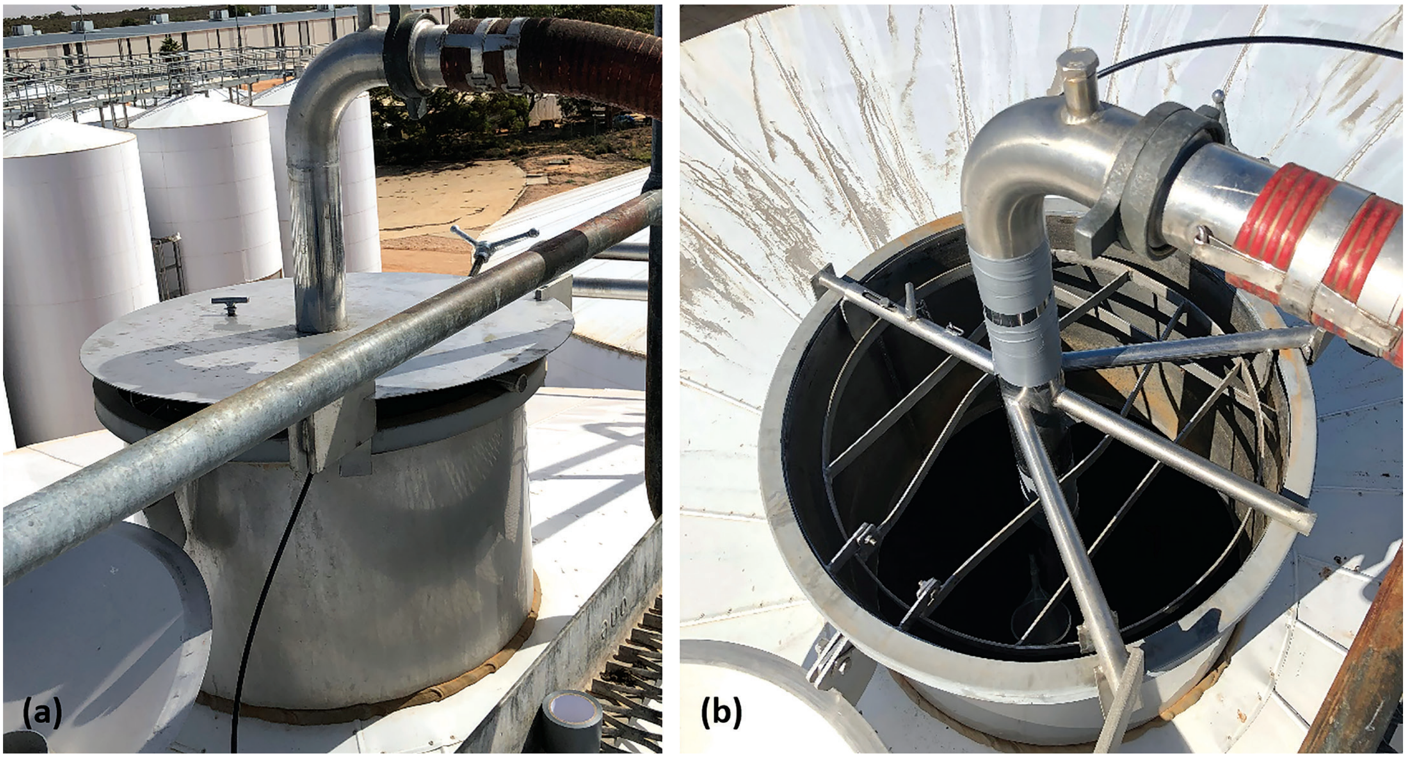

Figure 6. (a) Partially covered fermenter top, and (b) completely open fermenter top.

(Figure 3b) to try to prevent any drips of liquid running down the outside of the tube from being drawn in.

Verifying the sensing system's response to H_2S

Before deciding to continue experiments with the system for the 2020 vintage, some simple laboratory experiments were performed to verify that the H_2S sensing system was providing a response proportional to H_2S concentration. Model wine solutions containing 0.05, 0.1 and 0.2 mg/L H_2S were prepared (12% ethanol, 5 g/L tartaric acid, pH adjusted to 3.2 with sodium hydroxide, H_2S from sodium sulfide nonahydrate). The solutions were used to half-fill 10 L bottles with lids and agitated with magnetic stirrer bars to try to achieve an equilibrium between the H_2S dissolved in the liquid and that in the headspace. In a randomised order, the headspace of each bottle was then circulated through the H_2S sensing system via resealable holes in the lid on each bottle.

The experiments demonstrated that the system did output values proportional to the H_2S concentration (Figure 5). The relationship was very close to the partitioning of H_2S between the liquid and the headspace expected from a previous study (Mouret *et al.* 2015).

Vintage 2020 – More air-purging and measuring carry-over

In 2020, vintage experiments were performed at another winery in red

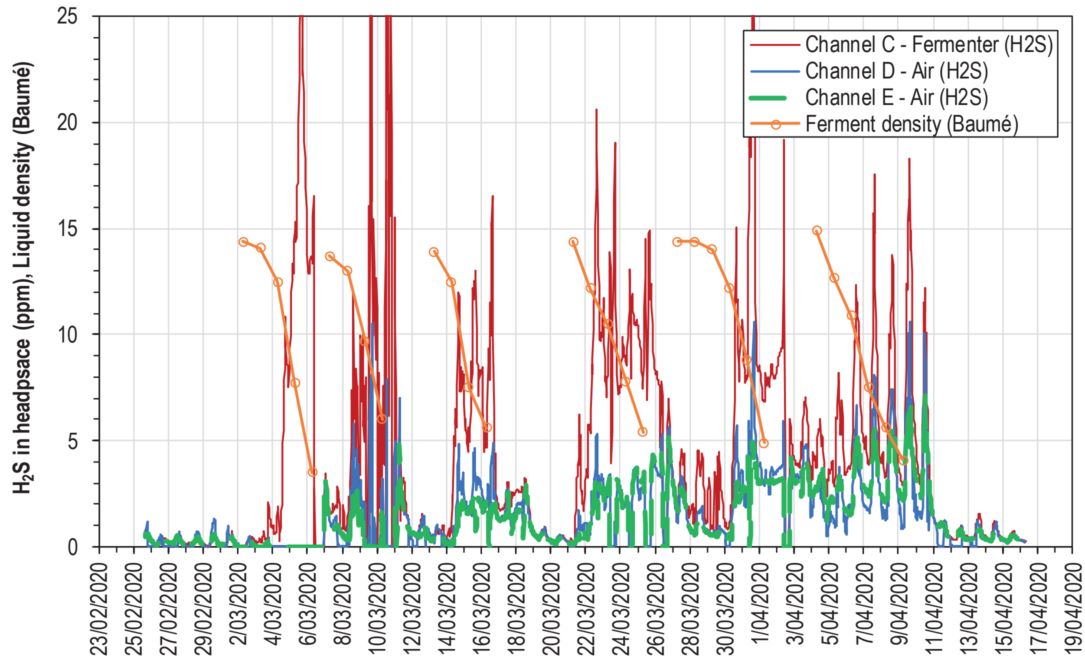

Figure 7. Assessment of carry-over of measured H_2S between sampling channels by having sampling channel C in the ferment headspace but the following channels D and E just sampling ambient air from near the fermenter (during six ferments in vintage 2020,°Baumé data shown where available).

fermenters typically holding around 300 t. Several conditions were trialled to try to better understand the results from the 2019 vintage, particularly the unexplained daily periods where there were readings of zero H_2S. Only two of the sensing system's five sampling channels (A and C) were used on fermenters, with the remaining channels (B, D and E) taking in air to allow greater purging of the system and gain an understanding of the carry-over of results between the sampling channels. To try and rule out the possibility that UV light during the middle of the day could have been responsible for the zero H_2S readings in 2019, translucent sample tubing was replaced with black tubing and one of the two fermenter was fitted with a cover to partially shield the headspace from direct sunlight, while still allowing ferment gas to escape (Figure 6).

The daily periods of zero H_2S from 2019 did not occur regularly during the 2020 trials for either the partially or totally open tank. It seems likely that the greater air purging used in 2020 was responsible for this improvement. Electrochemical H_2S sensors require oxygen at the counter-electrode for correct operation (Figure 8). This is a major consideration in monitoring ferments where the ferment gas is predominantly carbon dioxide and contains negligible oxygen. The extra air channels showed significant carryover of the H_2S results between channels that worsened as the vintage progressed (Figure 7). Longer air purge times or another means of providing oxygen to the system are probably needed.

While in 2020 there were no longer the regular unexpected zero H_2S readings in the middle of each day, there were still significant daily fluctuations in H_2S data that tended to obscure what the ferment's

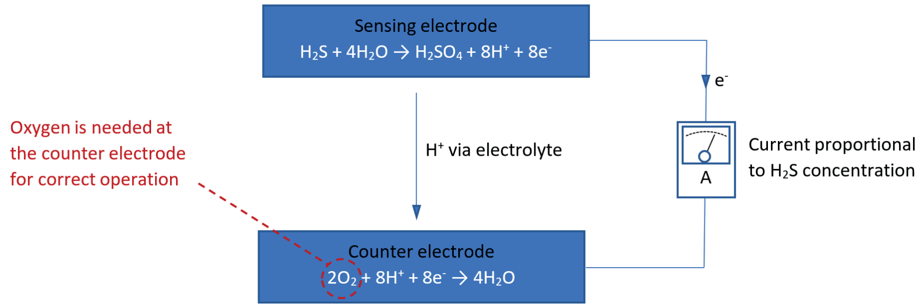

Figure 8. Simplified representation of the chemical reactions in an electrochemical hydrogen sulfide sensor (adapted from Chou 2000, Alphasense 2013, Figaro 2019).

H_2S level was. These daily fluctuations tended to be correlated with temperature and might potentially be resolved by altering the temperature compensation factor used by the system.

At the end of the vintage, red residues were again found inside the system, suggesting that some fermenting juice had still been drawn up at some point, despite the modifications made to prevent this (Figure 3b).

Ultimately, the system being tested was a packaged system and it was not possible to change settings for parameters such as purge time and temperature compensation that might improve system performance. The concept of using H_2S sensors is still of some interest because it should correlate with what winemakers smell. However, more development and validation work would be required to provide the confidence to rely on electrochemical gas sensors in this application. The specific sampling configuration would also need to be carefully considered. Avoiding getting liquid into headspace gas sensing systems may be difficult in a winery environment where other operations occur above tanks. Sharing sensors between tanks via tubing is probably also not ideal, as while it makes a sensing system more affordable, tubing is at risk of crimping or blocking, resulting in erroneous results.

Figure 9. An ORP Probe (Endress + Hauser CPS72D).

Oxidation-reduction potential (ORP/redox) probes

Oxidation-reduction potential (also known as redox potential) is another measurement technique that may be useful for managing H2S production during fermentation and has received some recent attention (e.g. Boulton 2016, Boulton 2019, Walker 2020) including in relation to controlling the quantity of air injected into ferments (e.g. Killeen *et al.* 2018, Wilson 2018, AWRI workshop 2021).

Oxidation-reduction probes (e.g. Figure 9) look similar to pH probes, but while a pH probe measures the activity of hydrogen ions, an ORP probe measures the activity of electrons, with results recorded as a voltage reading that describe the relative potential for oxidation and reduction reactions to occur. Reductive reactions are more likely to occur at more negative mV, including some that may contribute to H_2S production. Maintaining the ORP at higher levels through aeration or other techniques may therefore be desirable.

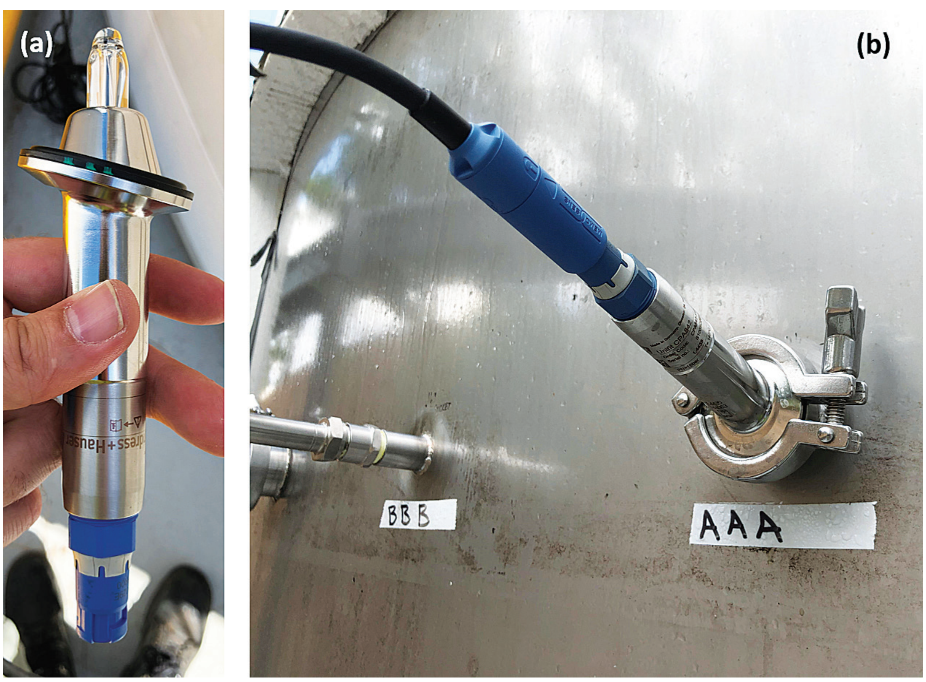

Figure 10. Installation of the ORP probe: (a) probe inside 15° angle assembly, and (b) with that assembly connected to the tank with a tri-clamp.

During the 2021 vintage, ORP probes were installed on two 228 kL white ferment/storage tanks to gain some experience with this measurement technique. One of these tanks was the same one used in previously reported trials of pressure sensors and radar for monitoring liquid density and level (Nordestgaard 2021). The Endress+Hauser CPS72D ORP probes were installed approximately 1.5 m from the floor of the tanks on a 15°

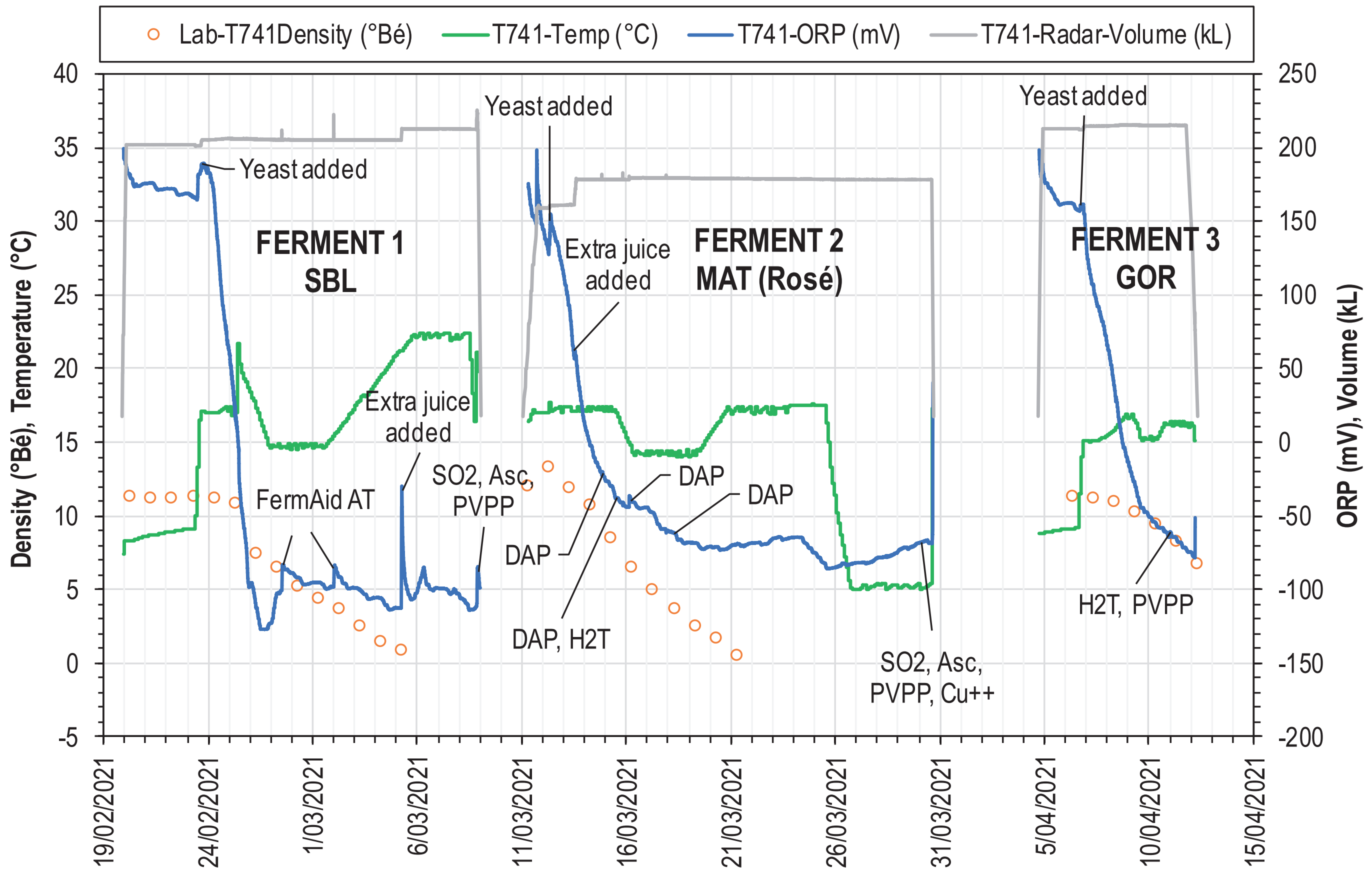

Figure 11. Oxidation-reduction potential (ORP) and other parameters measured during three ferments, with approximate timings of additions marked (SBL – Sauvignon Blanc, MAT – Mataro, GOR – Muscat Gordo Blanco).

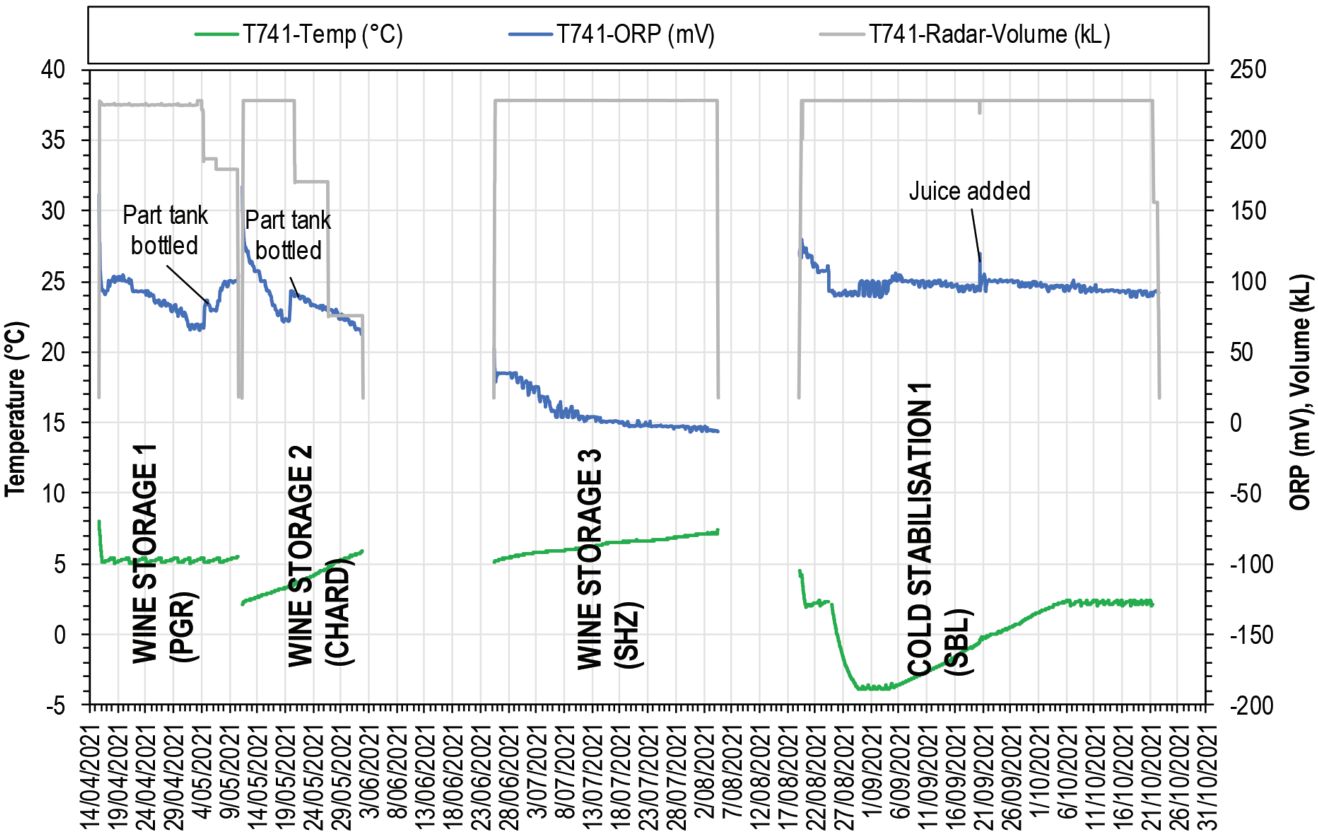

Figure 12. Oxidation-reduction potential (ORP) and other parameters measured during wine storage (PGR – Pinot Grigio, CHARD – Chardonnay, SHZ – Shiraz, SBL – Sauvignon Blanc).

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angle using a specific assembly (Figure 10).

Juice ORP was typically 150 to 200 mV but dropped quickly during fermentation down to -50 to -120 mV (Figure 11). Metabolism in microbial cells is known to play a significant role in setting ORP levels (Kukec *et al.* 2002). There were various small spikes in the ORP during fermentation, many of which seemed to correspond with additions being made to the tank. It is likely that these generally related to aeration occurring during the pump-overs that were used to mix in the additives rather than the additives themselves.

During later wine storage ORP values were between -10 and 120 mV (Figure 12). The one red wine tested had the lowest ORP. Spikes in ORP were seen when portions of tank contents were removed for bottling, and there was a tendency for ORP to decrease slowly during storage. It is possible that this related to the consumption of small quantities of oxygen that had been added when wine was pumped into or out of the tank.

The digital ORP probes did not have to be calibrated before use. At the end of October 2021, their accuracy was checked against a nominally 220 mV buffer solution and they were found to still be reading very accurately despite having been left in the tank from February to October. While ORP probes look like pH probes, they are generally more robust, but can still be damaged if they are not kept wet and the reference system dries out.

This study did not involve any intentional aeration to alter ORP, but other researchers at the AWRI have worked specifically on the benefits of aerating ferments. More information can be found in the 2020 webinar by Dr Simon Schmidt and the recent panel webinar hosted by Matt Holdstock featuring presentations by Luke Wilson, Jeremy Nascimben, Prof Roger Boulton and Antonio D'Onise, available on the AWRI's YouTube channel. An extension package on the topic of ferment aeration will also go live on the AWRI website around the time this article is published.

Conclusions

This article presents some initial experiences from trials of electrochemical H_2S sensors and ORP probes. The H_2S sensing system trialled showed some promise but suffered from fluctuating results, partly relating to insufficient air purging of the system. It would need more development work before it could be relied upon. ORP probes showed similar fermentation trends to those in previous literature reports. The interpretation of ORP data and its relationship with H_2S production appears likely to be more complex than for established winery parameters such as density, but it is still interesting because it is an instrumental approach that could be used for process control, instead of relying on sensory analysis.

Acknowledgements

This project is supported by Australian grapegrowers and winemakers through their investment body Wine Australia, with matching funds from the Australian Government. The AWRI is a member of the Wine Innovation Cluster in Adelaide. The equipment suppliers are thanked for providing the sensors for the trials, as are the wineries collaborating with the AWRI on ongoing sensor trials. Allie Kulcsar and Dr Marlize Bekker are also thanked for help with preparation of H_2S solutions.

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