Mercaptans and other volatile sulfur compounds in wine

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An article on volatile sulfur compounds in wine isn't likely to turn many heads. In truth, it's the sort of topic that gets filed away as 'worthy but dull', and only ever gets read by people who are swotting up for their diploma or MW, and then gets promptly forgotten. Aware of this, I'm willing to strike a deal with my readers. If I try my best to cover this otherwise fiercely dull and technical wine science piece in a manner that is both readable and doesn't require any specialist science knowledge, will you try to venture below the first paragraph?

Volatile sulfur compounds, and specifically mercaptans, are a hot topic in wine at the moment, so it's worth learning a bit about them. These are the compounds largely responsible for the olfactory defect known as 'reduction'. And there's a lot of ignorance and misinformation appearing about them, even in print. My aim in this piece is to present a step-by-step guide to these molecules in wine, bringing in some of the latest research and providing an accessible introduction to the subject without skimping on the meaty bits.

There are around 100 volatile sulfur compounds that have been identified in wine, but only a few are significant enough to be included in our story here. What do you need to know about them? First and foremost, they are smelly. Thus even at low concentrations they can have a sensory impact on the wine. Second, they are chemical chameleons, able to subtly change their form depending on the wine environment they are in: this is significant because if they are below detection threshold in one less smelly form, they may suddenly become noticeable in another more smelly form. Third, they aren't all bad: recent research has shown that they are important contributors to varietal character in many wines, so winemakers should be careful not to just eliminate them randomly.

Reduction

'Reduction' is the term used to describe the presence of volatile sulfur compounds in wine. It's actually a bit of a misnomer. Let me try to explain why. Reduction and oxidation are two different chemical processes that complement each other. In a chemical reaction, electrons change hands, and as one compound is oxidized another is reduced. If there is plenty of oxygen around, then chemical components in a wine will be gradually oxidized (the electrons are transferred from the chemical components in the wine to the oxygen). The end result is an oxidized wine. During fermentation the yeasts need oxygen, and in the early stages of red wine development a little oxygen is helpful because it allows the oxidation of some ethanol to acetaldeyde (also known as ethanal) which can then help with the development of tannins and pigmented polymers that are important in building structure and colour (this is the theory behind microoxygenation). But after this, wine development is largely reductive: that is, it occurs best in the relative absence of oxygen.

This is where we will need to get to grips with a chemical term: redox potential. This is a measure of how oxidative or reductive a system, such as a wine in barrel or bottle is, and it is measured in millivolts (mV)—the higher the reading, the less reductive. Typically, an aerated red wine will have a redox potential of 400–450 mV, whereas storage in the absence of air for some time will reduce this to 200–250 mV. If levels get as low as 150 mV then there is a danger that reduction problems can occur. Exposure to oxygen through winemaking practices such as racking, topping up barrels and filtering, increases the level of dissolved oxygen in the wine and increases the redox potential, which will then return to 200–300 mV. In white wines, this redox level will change much more rapidly than red wines, because red wines have a higher concentration of phenolic compounds such as tannins which are able to interact with oxygen, and act as buffers. Another variable here is the level of free sulfur dioxide in the wine, which will act protectively by reacting with the products of oxidation. Yeast lees also scavenge oxygen and protect the wine in a similar fashion, helping to lower the redox potential and create a more reductive environment. In modern winemaking, reductive conditions are encouraged: the protection of wines from oxygen by the use of stainless steel tanks and inert gases helps to preserve fresh fruit characters.

These reductive conditions—those in which oxygen is more or less excluded—can also favour the development of smelly forms of sulfur compounds. This is where thee term 'reduced' comes from, and if this 'reduction' occurs before bottling, addition of oxygen may correct the fault. But it is important to note that these sulfur compounds can develop in wine even in non-reductive conditions, at which stage further oxygen exposure may result in turning a smelly wine into a smelly oxidized wine. Equating the term 'reduced' with the presence of volatile sulfur compounds is therefore an oversimplification. In fact, when people use 'reduction', they are actually referring to the presence of sulphur compounds. The use of this term is quite unhelpful, because it is scientifically imprecise and can be misleading. '"Reduction" is a simplification, a language abuse,' says Dominique Delteil, scientific director of the ICV in the south of France. 'As often occurs in wine vocabulary, tasters have been willing to link sensory sensations to chemical or physical states, without being sure they are real or not. Reduction is typical of this.' Delteil continues, 'I prefer to call this concept "sulfur flavours" rather than "reduction".' Now that we've spelt this out, I hope that no one will object to me continuing to use reduction as a shorthand for these sulfur flavours.

Volatile sulfur compounds: a quick tour

So what are the characteristics of reduction? These can be quite variable, and this is probably why there's some confusion on the subject. Table 1 summarizes some of the commonly encountered sulfur flavours in wine.

TABLE 1 Some of the volatile sulfur compounds in wine

Compound	Sensory impact	Notes
Hydrogen sulfide	Rotten eggs, sewage	This is the main baddy, made by yeasts when they use one of the sulfur-containing amino acids as a nitrogen source. Stress also encourages its formation.
Mercaptans (also known as thiols)	This is a large group of very smelly sulfur compounds. Terms such as cabbagey, rubbery, struck flint or burnt rubber are used as descriptors.	If hydrogen sulfide isn't removed quickly, it can result in mercaptan production. This is a big worry for winemakers.
ethyl mercaptan	burnt match, sulfidy, earthy	Often negative, but can be positive in the right wine environment at certain levels.
methyl mercaptan (methanethiol)	rotten cabbage, cooked cabbage, burnt rubber, stagnant water	One of the compounds implicated in screwcap reduction
dimethyl sulfide	Cooked vegetables, cooked corn, canned tomato at high	

	levels; blackcurrant drink concentrate at lower levels. Quince, truffle.	
diethyl sulfide	Rubbery	
carbon disulfide	Sweet, ethereal, slightly green, sulfidy	
dimethyl disulfide	Vegetal, cabbage, onion-like at high levels	
diethyl disulfide	garlic, burnt rubber	
4-mercapto-4-methylpentan-2-one (4MMP), 3-mercaptohexan-1-ol (3MH), 3-mercaptohexyl acetate (3MHA)	Tropical fruit/passion fruit at low levels; cat's urine at higher levels.	Common in Sauvignon Blanc but also found in red wines where they can contribute to the blackcurrant fruit aroma. An example of sulfur flavours that can be positive in the right environment.
benzenemethanethiol	Smoky/gunflint aromas	Can be positive in the right context and at the right levels

Where do these sulfur compounds come from in the first place? It's mainly from yeasts. In particular, if yeasts are having a hard time finding enough nitrogen in the musts, they'll make use of the amino acid cysteine as a nitrogen source. Cysteine contains sulfur, and this sulfur is recombined chemically by the yeast metabolism to form the smelly sulfur compounds that are the subject of this piece. It is of great importance, therefore, for winemakers to make sure that their yeasts are happy and have an adequate nitrogen supply. 'Yeast assimable nitrogen' is the technical term that's used here. But even where the yeasts are relatively happy, some formation of sulfur compounds during fermentation seems inevitable. And these compounds need careful handling by winemakers if they aren't to turn into problems.

Why sulfur compounds in wine is officially a hot topic
Volatile sulfur compound chemistry is a hot topic in wine for two reasons. First of all, the closures debate has pointed the finger at screwcaps in sealing wines so tightly that the resulting wine environment has a low redox potential that in turn encourages reduction. Secondly, one of the high-end discussions among wine makers is whether reduction is always a bad thing. Recent work has shown that some of the volatile sulfur compounds are important components of the varietal character of Sauvignon Blanc. They may also be important for other wine styles, too, and have also been isolated from wines made with Gewürztraminer, Riesling, Colombard, Petit Manseng, Semillon, Cabernet Sauvignon and Merlot, among others. And there's some interesting evidence that 'reduction' at a low level, in the right wine contexts, may be an important complexing factor. Could it even be that what we think of as minerality in wine, which we attribute to the soil—terroir, if you will—could all be about volatile sulfur compounds? Now there's a thought.

Let's first correct a popular misconception, though. Sulfur dioxide (SO_2) is not a volatile sulfur compound, and is not really part of the 'reduction' syndrome. SO_2 is added to wine in order to provide microbiological stability, and perhaps more importantly to prevent oxidation. Actually, it's a little more complicated than that. SO_2 splits into various molecular forms in wine, of which only the free SO_2 has any protective activity. It reacts with oxygen only slowly, so in actual fact its role is to bind up the products of oxidation in wine so that the oxidation isn't apparent, even though oxidation of the wine components will already have occurred. This is a complicated, but important story, but it isn't terribly relevant to our discussions here.

Now the really controversial bit. Can you believe it? Sulfur compounds in wine—'reduction'—has been in the national press in the last few weeks. The *Daily Telegraph* carried a story titled 'Screwcaps blamed for tainting wine' on 19th September, which was also picked up by other news outlets. This was prompted by the results of the faults clinic from the 2006 International Wine Challenge (IWC). 'In a number of cases the IWC chairmen validated a link between screw cap use and a unfavourable vegetal/rubber flavoured compound—presumed to be a complexed sulfide', reports Sam Harrop MW, who was one of the four IWC chairs. 'At first glance a percentage of 4.9% of total faults may not seem high, but when examined in the context of total screw cap figures, a more worrying rate of 2.2% [of all screwcapped wines] emerges. In the context of the 2006 IWC cork taint figure of 2.8% [of all natural cork-sealed wines], this fault type is significant and should be given more attention by wineries using screwcap.' However, Harrop is keen to emphasize that he's not equating the two: 'While the IWC figures for screwcaps are a concern, there is no question in my mind that the continued incidence of cork taint is still a more serious issue.'

The potential problem with sulfides in screwcapped wines first came to the wine world's attention through the magnificent closures study began by the Australian Wine Research Institute (AWRI) in 1999, and which has been reported on at regular intervals as the wine (a 1999 Semillon from the Clare Valley) has developed under a range of some 14 different closures. Included in this study was a metal-lined screwcap. The liner is important here: the oxygen transmission properties of a screwcap are determined by its nature. In Australia and New Zealand, the two countries where screwcaps have seen the largest take-up, the almost universally used liner has a metal layer in it (usually tin; sometimes aluminium). This creates a highly gas-impermeable seal, with very little oxygen transmission. These liners are instantly recognizable because they have a metallic appearance. The other commonly used screwcap liners for wine appear white—these are known as saranex-only liners and allow more oxygen transmission, although probably a bit more than is needed just to avoid reduction, and likely more than we'd want of a closure for wines destined for keeping for more than a few years.

In the first major report from this closure trial, 20 months on, the AWRI reported that the tin-lined screwcaps performed as expected: with their tight seals they kept the wine freshest, and the screwcapped bottles scored highest for fruity aromas, maintaining the highest levels of free sulfur dioxide while showing the least colour development. But they also scored highly for 'struck flint/rubber' in the sensory analysis. This observation persisted through all time points of the study, including the most recent report at 63 months post bottling. Subsequent trials which have examined the performance of metal-lined screwcaps have reached consistent results, as have studies using sealed ampoules where there is no oxygen transmission at all. 'Reduction' seems to be a problem in these sorts of analytical studies involving metal-lined screwcaps. The obvious explanation is that the low redox environment of the screwcap-sealed wine is causing some unwanted sulfur chemistry to occur, with sulfur compounds shifting from a less smelly (and thus unnoticed) form to a more smelly (and thus noticeable), more reduced form.

What are we to make of this? Is it a real world problem on a part with cork taint, or is it just a minor technical problem—a teething issue that just needs a bit of tweaking? The latter position has been the one consistently adopted by proponents of screwcaps. Indeed, quite a number of individuals and wineries have aligned themselves strongly with this closure type by signing up to the International Screwcap Initiative. They have invested a fair bit of emotional energy in this cause, as well as several years' production of their wines, so their natural response to these sorts of data is to either fight or deny them. Others have been gunning for screwcaps to fail—none more so than the cork industry who see their livelihood threatened by this remarkably easy-to-use (from the consumer's perspective) closure.

Since the publication of the first AWRI report in 2001, there has been just a trickle of data on the subject of screwcap reduction. But little by little a clearer picture has emerged, and I would go so far as to say that the current weight of evidence suggests that the issue of mercaptans in screwcapped wines is problematic enough that some caution should be exercised in their use. First we have the consistency of the observation: where people have been looking carefully at screwcapped wines, these mercaptans (or what people believe to be mercaptans from sensory analysis) have always been found.

Then we have anecdotal observation by interested parties. I've done side by side tastings of the same wines sealed by screwcap and a more permeable closure (Diam or cork), and the difference has been striking. Of course, the value of this sort of observation depends on your view of my palate and intellectual independence. But I was personally convinced that there was a consistent character appearing in the screwcapped wines, which, while I probably would not have noticed it on its own if I hadn't been looking, appeared detrimental to the wine quality when made evident in the side-by-side comparison.

Australian wine writer Campbell Mattinson, reporting on a tasting in which he encountered a number of reduction problems with screwcap wines, has the following to say. 'Excessive reduction in a wine is a winemaking issue, not a closure issue. I know this. I've been told it 357 times—at least. Right. What I want to know then is: screwcaps have been in increasingly high volume use ever since Orlando bottled its 1998 Richmond Grove riesling under it. It's now 2006. How long, en masse, is it going to take for winemakers to get it right? When is the "winemaking issue" going to end? Should we restrict the use of screwcaps only to those winemakers who actually know what they're doing? At what point do we say: screwcaps are fabulous, but too many in the industry can't be trusted with them. Do we need to introduce a Screwcap Licence system?'

A recent comparative tasting of screwcapped and cork-sealed bottles was reported by Ralph Kyte Powell in Australian newspaper *The Age* (21 February 2006). 24 wines were tried, white and red. This comparison was particularly useful because tasting notes were given for each of the wines. Reading these notes, two points are emphasized. First, that the wines taste quite different in almost every case. Second, that the number of descriptors indicative of the presence of mercaptans in the screwcapped wines is striking. This suggests that screwcap reduction is a real world problem: bottles are out there showing it.

New Zealand winemaker (Stonecroft, Hawkes Bay) and PhD chemist Alan Limmer has been a bit of a thorn in the side of the screwcap lobby. He has written widely on the subject, bringing his knowledge of wine chemistry to bear. In particular, Limmer has pointed out that screwcap reduction is not a problem that can be completely eliminated by better winemaking, as many have claimed. 'In essence we are talking about thiol accumulation, post-bottling, from complex sulfides which do not respond to pre-bottling copper treatment,' claims Limmer, in response to the assertion that fining with copper removes reduction defects. 'This reaction occurs to all wines containing the appropriate precursors, irrespective of closure type. But the varying levels of oxygen ingress between closures leads to significantly different outcomes from a sensory point of view.'

Limmer's explanation for screwcap reduction is that sulfides present in the wine at bottling necessitate a very small level of oxygen ingress through the closure, otherwise they can become reduced to thiols. Because sulfides are less smelly, it is possible for a wine that is clean at bottling to taste reduced after bottling if the closure doesn't permit enough oxygen ingress. So the use of a closure, such as cork, which does allow a little oxygen ingress (but not too much) is a necessary concession to the vagaries of sulfur chemistry. Of course, we'd rather not have the sulfides in the wine at all, which would then avoid problems with reduction to mercaptans at a later stage. But, as Limmer points out: 'Controlling ferments to not produce the complex sulfides is beyond our means currently. This sulfide behaviour of the ferment is more controlled by the yeast genetics than the winemaker,' he explains. 'It is not the winemaker's fault these compounds exist in the wine at bottling. We can minimize it to some extent by providing optimum nutrient conditions for the ferment, and employing some specific winemaking regimes. But, the research tells us this only has a slight impact on the complex sulfide pattern produced by the yeast.' Limmer reinforces his point: 'The patterns are quite specific to each yeast type, almost irrespective of nutrient conditions. Every wine contains these complex sulfides.'

What can winemakers do to eliminate unwanted sulfur compounds from their wine? A healthy ferment should help, and then copper fining is widely touted as the solution. This certainly gets rid of mercaptans, but it doesn't eliminate disulfides which can, as we have seen, can revert in a low redox environment to mercaptans. For this reason, Limmer calls copper fining 'the Ambulance at the bottom of the cliff'. Besides, copper fining will also remove the desirable sulfides which are important for varietal character in Sauvignon Blanc and other grapes.

The new cork taint?

We have to be careful, however, not to overstate the potential threat caused by mercaptans in wines that are sealed by ultra-low permeability closures such as tin-lined screwcaps. The extent of screwcap reduction is currently unclear. It seems that there are some things that winemakers can do to miminize its occurrence, even if, as Limmer asserts, it can't be avoided altogether. The IWC data indicating that 2.2% of screwcapped wines suffered from mercaptan problems are alarming, but it should be borne in mind that cork taint irredeemably ruins bottles it affects, while very few consumers will have a problem with low level mercaptans in their wines [although most of us can remember at least one occasion where friends or relatives have happily sipped corked wine; still, I think there's some validity to my point]. I doubt that most of the wine trade would spot this as a problem in all but the most extreme cases, so it is unfair to equate it with the very well recognized problem of cork taint. Having said this, though, screwcap-sealed wines affected by mercaptans should be a major concern for winemakers because the closure is modifying the flavour of the wine, which is emphatically not reaching the consumer 'the way the winemaker intended'. It would be dangerously complacent for the industry to take the view that if the consumer doesn't notice it, then it doesn't matter.

Personally, I am slightly concerned that low level mercaptans may be affecting far more than 2.2% of wines sealed with screwcaps. 'They impact from an organoleptic perspective towards the end of the palate', claims Limmer, 'imparting a "mineral" or bitter/hard/astringent aspect. This has the appearance of shortening or closing up the palate, so the wine does not display a fine fresh long finish, but ends abruptly, and somewhat harshly.' This is describing something I've certainly noticed in side-by-side comparisons of cork and screwcap-sealed wines. Is it happening all the time, but going more-or-less undetected?

Gregor Christie of membrane cork company ProCork has been concerned enough about this problem that he has sent of wines for testing at ETS laboratories in California. Clearly, Christie has a commercial imperative for showing that ProCork is superior to tin-lined screwcaps in this regard, but even given this motivation, the results are interesting. Christie took the 2002 Clare Valley Semillon used in the commercial closure trial run by the AWRI, comparing ProCork with natural cork and screwcap, and submitted bottles sealed with all three closures to ETS for testing for a range of volatile sulfur compounds.

For methyl mercaptan, which has a perception threshold of 0.3 parts per billion (ppb), both the cork- and ProCork-sealed bottles were below detection limit. However, the screwcapped bottle showed a level of 0.6 ppb, above perception threshold.

But a sense of perspective is called for here. There's a real danger that the message that is distilled by journalists from all this technical talk becomes a misleading 'screwcaps taint wine' story. The picture emerging is a complex one, but such a simplification would be dangerous if it caused producers to back away from adopting alternative closure solutions, which would then have the knock-on effect of removing any incentive from the cork industry to put its house in order and do all it can to reduce taint levels. However, complications like this mercaptan issue should put pressure on winemakers to be more curious about the closures they are using. They should ask more questions about issues like oxygen transmission, and insist on seeing independently validated data on closure performance rather than accepting manufacturer's testimonials or sales pitches unquestioningly.