UNDERSTANDING AND MANAGING REDUCTION PROBLEMS

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Introduction

Reductive off-odors are a not infrequent outcome of wine production, particularly of bottle aging ([1-5]) and are responsible for an important proportion of faulty wines with nasty consequences for the brand image. Such a problem is mostly caused by the development of H_2S and Methanethiol (MeSH) ([4]), although a number of different other volatile sulfur compounds (VSCs) have been also identified ([1, 2]). A third relevant molecule, dimethyl sulfide (DMS), is also frequently included within the group of reductive problems. However, DMS strongly differs from H_2S and MeSH both in sensory effects ([6-8]) and in chemical origin and properties ([9]), and should be considered apart.

It is usually thought that the most relevant source of reductive off-odors is the alcoholic fermentation and in fact, the development of the characteristic H_2S and MeSH odors during this key wine making step is sometimes clearly observed. H_2S can be directly formed by Saccharomyces from elemental sulfur ([10]), sulfates or more easily from the sulfite ([11]) usually added as antioxidant and antimicrobial agent. The formation is typically stronger in musts with low levels of assimilable nitrogen ([11]), although the factors determining its synthesis are far for being clearly understood ([12]). In the event of an excessive formation of these compounds, winemakers try to control their levels by copper finning, aeration or addition of lees ([13-15]).

The reasons why these molecules accumulate during bottle aging, more often in those wines in which these compounds were previously formed in fermentation, are not clearly known ([14]). Several hypothesis have been formulated by scientists along the years, most of which have not been ever demonstrated. One of the hypothesis that has received more credibility among winemakers states that the origin of these compounds is the reduction of disulfides or of elemental sulfur ([16]).

This hypothesis likes everyone because is consistent with the observation that VSCs re-appear when the wine is stored without any contact with oxygen; i.e., in reductive conditions, and it is the hypothesis explicitly or implicitly accepted by renowned enology text books ([17, 18]) and wine consultants ([19]). The idea behind this is that the problem is a misuse of oxygen in previous stages of winemaking. During these stages, when O_2 comes in contact with wine containing H_2S and MeSH, what it is thought that happens is:

$$2H_2S + O_2 \rightarrow 2H_2O + 2\,S° \text{ (elemental Sulfur)}$$
$$2MeSH + \tfrac{1}{2}\,O_2 \rightarrow 2H_2O + MeS\text{-}SMe \text{ (dimethyl disulfide)}$$

Both elemental sulfur and disulfides are genuine oxidation products. Some authors even propose that disulfide production is enhanced when copper finning is carried out too soon after an aerative process, since it will act as catalyst ([19]).

Then and attending to such theory, these sulfur and disulfides will be further reduced. Reduction is the chemical term opposed to oxidation. If something is oxidized, it losses electrons (generally because O_2 takes them), while if something is reduced, it will take electrons. While it is not clear at all what is pumping electrons in, the truth is that the formation of H_2S from elemental Sulfur or of MeSH from its disulfide are genuine reductive processes:

$$S + H_2O \rightarrow SH_2 + \tfrac{1}{2}\,O_2$$
$$CH_3S\text{-}SCH_3 + H_2O \rightarrow 2CH_3SH + \tfrac{1}{2}\,O_2$$
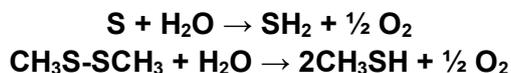
and that since H_2S and MeSH are much more odor active than elemental sulfur (odorless) or than disulfides (the odor threshold of dimethyldisulfide is more than 50 times higher than that of MeSH), this hypothesis seems to fit with winemakers experience.

Only that it is not true! Or at least it is not all the truth! As our findings will show

1st Finding. Wine contains H2S and MeSH in non-volatile and odorless forms

We have observed that the amounts of H_2S and MeSH measured in wine are extremely dependent on the method used for the analysis. Most methods measure the amount of these molecules present in the vapors above wine. These types of methods tell us how much of these molecules are volatile, but if these molecules would be bonded or anchored to something not letting them reach the vapor, these methods would not detect anything. We have developed a different type of procedure in which many of those "anchors" or "soft-bonds" are broken, making it possible to detect the molecules present as bonded forms. Combining the two types of methods it is possible to measure free forms (volatile and odorous) of H_2S, MeSH and other mercaptans and also bonded forms (non-volatile and odorless) (20).

Our results show that most normal bottled wines (not particularly oxidized or reduced) contain large proportions of H_2S and MeSH in those bonded forms. In average, we have measured that 94% and 47% of H_2S and MeSH are under bonded forms, as is summarized in table 1.

Table 1: Average, maximum and minimum fractions (in %) of H_2S , MeSH and DMS under bonded forms in bottled wines

Molecule	Average	Maximum	Minimum
H_2S	94% (red wines) 92 % (whites and roses)	99.9%	76% (reds) 83% (whites and rosés)
MeSH	62% (red wines) 31% (white and rosés)	83% (red wines) 60% (whites and rosés)	29% (reds) 4% (whites and rosés)
DMS	Not present in bonded forms		

2nd Finding. Each wine has a specific ability to bond REVERSIBLY H2S and mercaptans

If free H_2S and MeSH are added to different wines, it will be easily observed that there are some wines in which these molecules remain volatile, and hence can be easily smelled, while there are some others in which the molecules are so strongly bonded that they cannot be measured (and hence smelled) as free forms. Both patterns can be seen in Table 2. Wine 2 follow the first pattern and recoveries of free forms are very high, while wine 3 follows the second and free forms of H_2S are even not detected. However, the method for total forms confirms that these molecules still are in the wine (92% recovery), even though after some days they seem to be transformed in something else and the recovery drops.

Table 2: Recoveries of H_2S and MeSH spiked to two different wines. A recovery of 100% means that the signal measured fully corresponds to the complete amount of spiked compound (adapted from reference (20))

		H2S		MeSH	
Recovery (%)		Free	Total	Free	Total
Wine 2	after spike	108%	105%	101%	100%
	2 days latter	53%	103%	84%	100%
Wine 3	after spike	0.0%	92%	62%	100%
	2 days latter	0.0%	20%	6.6%	95%

3rd finding: H2S and mercaptans do not precipitate but form stable, reversible and soluble complexes with some cation metals, notably copper

The plot shown in Figure 1a (adapted from reference (20)) clearly indicates that some cations are perfectly able to bind free H_2S and MeSH avoiding their presence in the headspaces of wine.

Figure 1: 1a) Recoveries of FREE H_2S added to a synthetic wine sample containing 0.5 mg/L of different metal cations; 1b) recoveries of TOTAL H_2S and TOTAL MeSH added to a synthetic wine containing 0.5 mg/L of copper sulfate
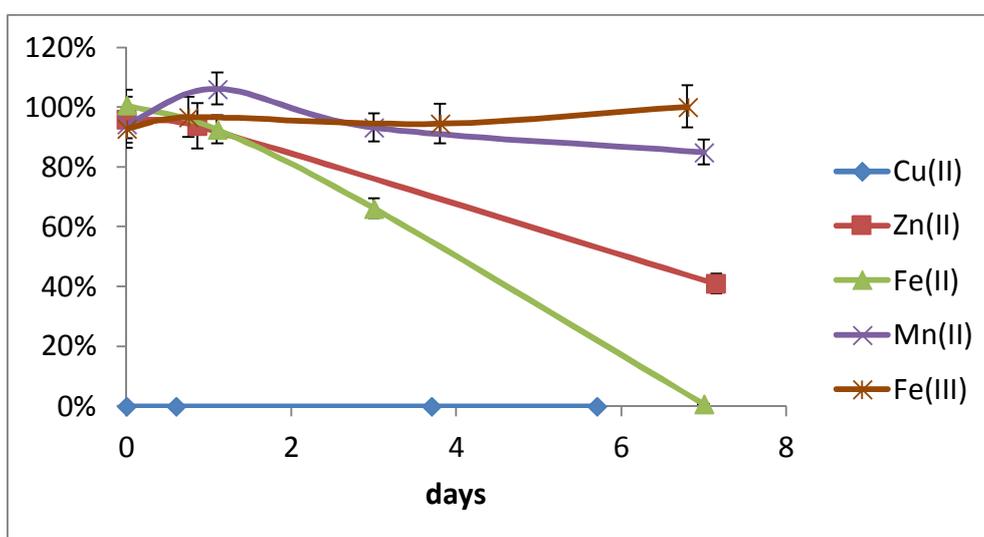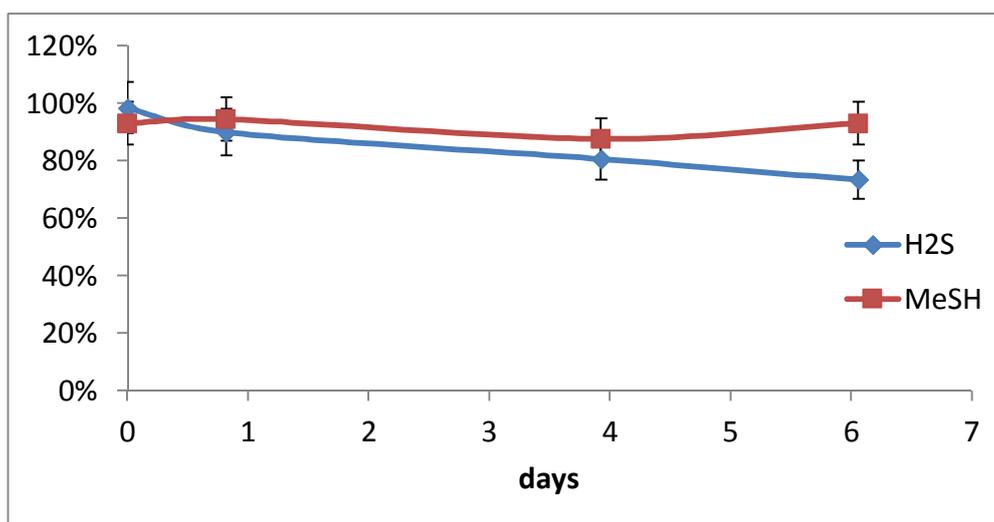
As can be seen in Figure 1a and in accordance with winemaking experience, a little bit of copper sulfate is enough to completely remove H_2S from the headspace. Results for MeSH (not shown) were similar. Ferrous ions (Fe(II)) were also able to bind H_2S but that was noticeable only after several days. Zinc was also able to bind smaller amounts of H_2S and it also required more time. All these results were not surprising.

What is new is the fact that H_2S and MeSH were in fact present in the synthetic wine containing copper even though the molecules in the headspace could not be detected (Figure 1a). In addition, we have been taught that Cu(II) and H_2S precipitate as CuS. However, the analysis of those samples containing H_2S, MeSH and copper sulfate with the method for total forms, revealed that most of both compounds were still in the solution as shown in Figure 1b. It should be remarked that no precipitation at all of any CuS was observed. We have confirmed this many times and we can ensure that CuS does not precipitate in normal wine conditions. Even at levels of H_2S and copper as high as 1 and 2 mg/L, respectively, there is no precipitation, which is essentially similar to what some Australian researchers have demonstrated that happens in wine (*13*).

This third finding may sound shocking, since it is the opposite to what we were taught in chemistry and enology textbooks (*17*). However, there is a sound explanation that has to do with the chemistry of highly diluted solutions. At the low levels at which H_2S and Cu(II) are found in wine, what it is formed is not a separated solid salt of CuS, but a series of "clusters" containing basic units of Cu_3S_3 (*21*). Those clusters are to the solution something similar to what fog or smoke are to air. They can stay as truly solved molecules, or they can act as colloids or even as nanoparticles, but they do not form a separate phase. These types of clusters formed by a metal cation and a sulfide are really ubiquitous in nature and, are among other things, responsible for the fact that oxygen-sensitive sulfides can endure even in oxygenated waters (*21-23*). They are also responsible for the aqueous transport of supposedly insoluble cation metals in different environments (*24*) and some studies reveal that in fact, the formation of soluble sulfides is a clever strategy used by some species to detoxify from toxic metals (*25*).

The key aspect to understand is that H_2S and MeSH strongly bonds Cu(II), but not to form a separated solid phase, but forming some kind of soluble or colloidal sulfides that remain in the wine constituting a concealed pool for those two malodorous compounds.

4th finding. The wine content in wine metals perfectly explains the wine content in total H_2S

It may sound weird, but we have been able to derive some mathematical models predicting with accuracy the content in total H_2S of a wine just taking into account its content in cation metals (some more chemicals are required in red wines). In the case of whites and rosé wines we have come across the following relationship:

$$\text{Total } H_2S \text{ content} = k_o + k_1 C_{Cu} + k_2 C_{Mn} - k_3 C_{Fe} - k_4 C_{Zn}$$

While there are some elements in the equation that we cannot yet explain, it is remarkable that it suggests that the copper present in the fermenting must may act as a kind of trapping system for the H_2S which otherwise would have been blown off the fermenting vessel by the CO_2 released. Similar results are obtained for red wines. The role of the other cations is not clear but they should be related to some catalytic activities of yeast enzymes.

5th finding. The increments of free H_2S observed when wine is stored in anoxia are mostly due to the release of complexed forms. In the case of MeSH, de novo formation is most relevant (>50%)

This can be clearly observed in Figure 2a, which summarizes what happens to the free and total levels of H_2S in red wines stored under strict anoxia for nearly 18 months. As can be seen, the levels of total forms remain constant along the whole period, while the levels of free forms increase slowly but continuously; indicating that the increases in H_2S observed along the anoxic storage of wines is mainly the consequence of the cleavage of the bonded forms which are released as free forms. Our results suggest that red wines release around 0.4 µg/L of free H_2S per month in average. Results for whites and rosés are similar, although in these types of wines the amount released is higher (around 0.7 µg/L/month). Differences between wines as regards their ability to accumulate free H_2S along the anoxic storage can be close to one order of magnitude.

The behavior of MeSH is quite different, as can be seen in Figure 2b. In this case there is also a continuous increase of free forms with storage time. In average, the accumulation of this powerful odorous molecule is 0.08 µg/L/month, which is around 1 µg/L/year for red wines. In whites and roses and in average, the increase of this molecule is around 1.7 µg/L/year. Differences between wines attending to their differential ability to accumulate free MeSH can be of factors above 6.

A relevant difference with the case of H_2S is that total forms of MeSH also experiment a notable increase, which was not observed in figure 2a. The magnitudes of those increases of total forms are similar to those of free forms. This means that in this case two different phenomena are taking place. On the one hand, there is a net release of free MeSH from bonded forms, but on the other hand, it is evident that all wines are able to form this molecule "de novo" from one or several precursors. Our data support the idea that the amino acid methionine remaining in the wine after the fermentation is one of the most important precursors for the formation of this molecule (*26*).

Figure 2: Average contents (µg/L) of total and free forms of H₂S (2a) or of MeSH (2b) of 13 different red wines stored under strict anoxia for 18 months
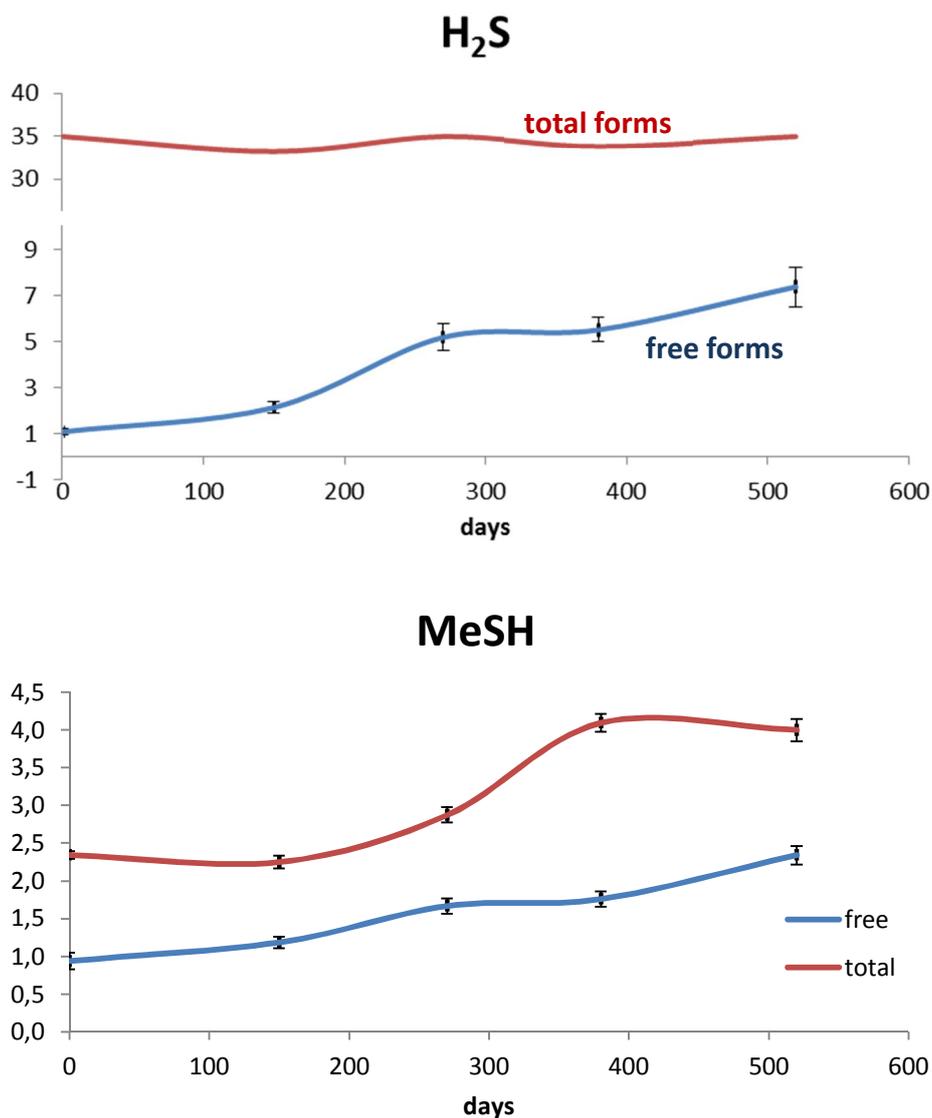
6th finding. Other relevant changes suggest that release of H₂S and MeSH may be caused by complex cleavage after the reduction of Cu(II)

Two other important chemical changes are observed during the storage of the samples in anoxia: a decrease in the redox potential and important increases in the Absorbances at 420 nm. Both changes seem to be strongly correlated, so that any increment in Absorbance is paralleled by a decrease in the redox potential, which becomes more negative (reductor).

In spite of the fact that within the scientific community there is some controversy about the true meaning of the redox potential (27), we think that the relationship between both variables is of causality; i.e., we think that redox potential decreases because some wine polyphenols are spontaneously experimenting some chemical reactions in which electrons are released (self-oxidation). These reactions involve the formation of more condensed forms of polyphenols which in turn imply an increase in the Absorbance at 420 nm (yellow color). This is something that most often is neglected: some polyphenol condensation reactions are in fact self-oxidation reactions since they involve the release of electrons. If O_2 is present in the media, these electrons will be taken by O_2.

However, when that phenomena takes place in strict anoxia, these electrons will increase the ratio Fe(II)/Fe(III) of the wine, making its redox potential to become more negative. The hypothesis is that at some point of the process, the accumulation of electrons is enough to reduce Cu(II) to Cu°. In this way, any H_2S of mercaptan bonded to Cu(II) would be released.

This hypothesis still requires a direct experimental confirmation, but it is consistent with the facts. It is also consistent with the models that we have obtained explaining the accumulation of free H_2S and MeSH attributable to the release from bonded forms. In all the cases the models show the following structure:

$$\text{Released } H_2S = k_1 + k_2 \, H_2S_{bonded}/Cu + \ldots$$

$$\text{Released MeSH} = k_3 + k_4 \, MeSH_{bonded}/Cu + \ldots$$

The models reveal that the release is proportional to the pool of bonded forms trapped in the wine and inversely proportional to the amount of copper that the wine contains. This is a little bit of a paradox, since in a previous finding we saw that the amount of H_2S contained in the wines was proportional to its copper levels (4th finding). What happens is that copper traps so strongly H_2S and mercaptans that makes their release more difficult. Then it follows that if our wine contains more copper, it will also contain more H_2S, but it will release it at a slower rate.

But still there is more!

7th finding: The "de novo" formation of H_2S and of MeSH takes place through the copper catalyzed desulfuration of S-amino acids

In a previous finding (5th finding) the "de novo" formation of MeSH was reported to be a normal wine process. This was not the case of H_2S, for which the novo formation is observed only in some particular wines and in some particular storage conditions. Our data suggest that de novo formation of H_2S is mostly inhibited in red wines, but that it can be active in whites and rosés, being strongly accelerated by high storage temperatures. Models explaining such de novo formation again attribute to copper an important role. Such a role has been confirmed by working with synthetic wine models containing amino acid precursors, copper and some polyphenols, as illustrated by Figure 3.

Figure 3: Effect of the presence of copper in the total contents of H_2S and MeSH of a synthetic solution containing amino acids and wine phenols and stored in strict anoxia at 50ºC (work carried out by Ricardo López and Sandra González)
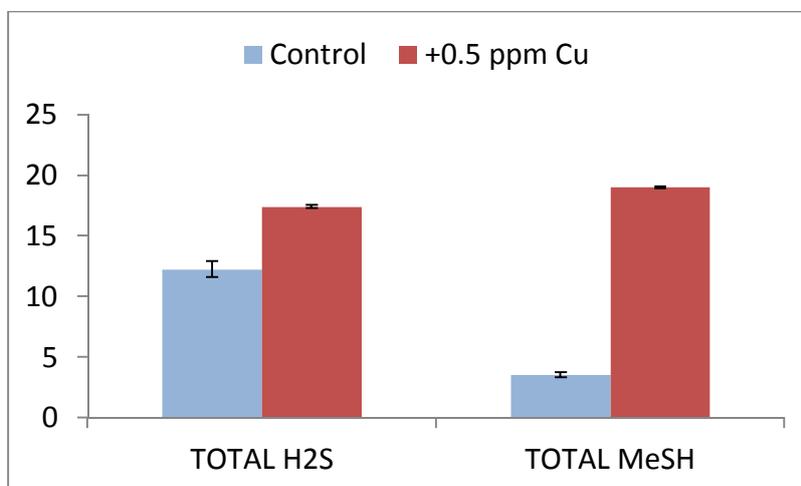
These observations raise several questions about the usefulness and risks of copper fining. In order to investigate this a little bit more, we treated a young red wine affected by a reductive off-odor with three different dosages of copper, including one well known commercial Cu-finning aid specifically designed for this purpose. Results are summarized in Figure 4.

Figure 4: Copper finning on a young red wine affected by a reductive off-odor. Effects of the treatments on the levels of free forms of H_2S and MeSH (work carried out by Eduardo Vela and Purificación Hernández-Orte)
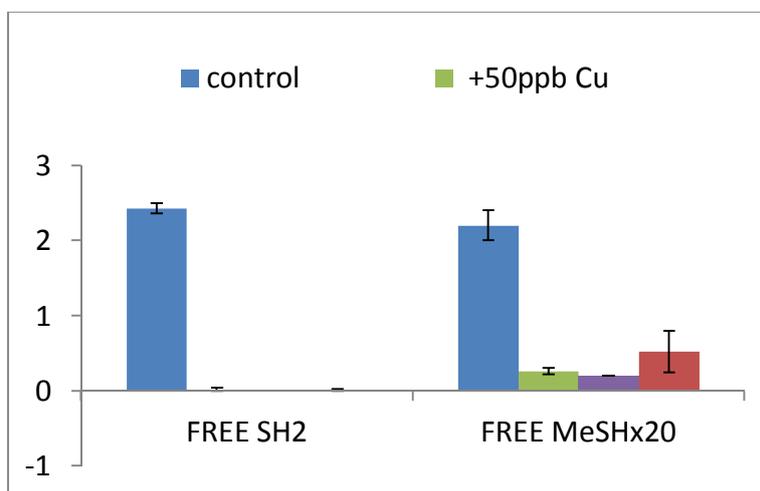
The analysis of free forms revealed the presence of little amounts of H_2S and MeSH in the headspace of the problematic wine and confirmed the drastic effect exerted by any form of copper finning on those free levels, as shown in Figure 4.

The surprise came when we analyzed the total forms of the wine after the different treatments that lasted just 3 weeks. These results can be seen in Figure 5.

Figure 5: Copper finning on a young red wine affected by a reductive off-odor. Effects of the treatments on the levels of total forms of H_2S and MeSH (work carried out by Eduardo Vela and Purificación Hernández-Orte)
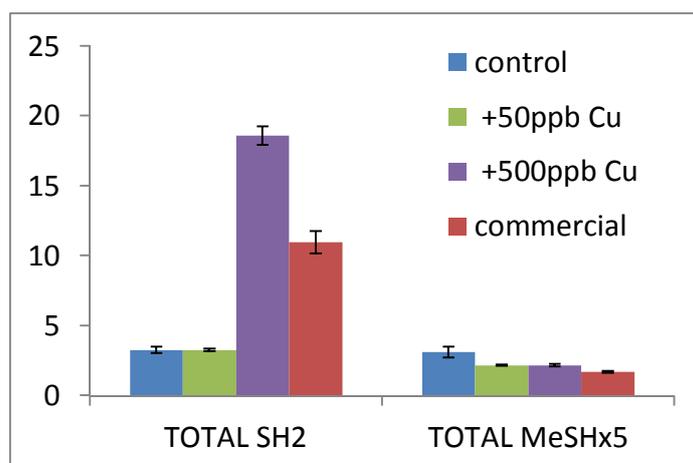
As the figure reveals, the total levels of H_2S strongly increased in the samples treated with the commercial Cu-finning aid (used at the suppliers recommended dose levels) and in the treatment with high levels of copper. The treatments did not significantly affected total MeSH levels. Both plots

clearly illustrate the benefits and potential dangers of copper finning. On the one hand, as shown in Figure 4, there is an immediate decrease of free levels, so that the off-odor is no longer perceived. On the other hand, as shown in Figure 5 and also in Figure 3, H_2S and MeSH have not been really removed from the wine, rather they have been concealed as bonded forms; but worse, the catalytic abilities of the wine to produce de novo H_2S and eventually MeSH may have been promoted. These results suggests that the effects of copper finning are a bit those of a Russian roulette.

8th finding. Not all the Oxygen is equally efficient at removing H_2S and mercaptans

In fact, only the oxygen taken at relatively low dosages during extended periods of time, such as those typical of extended micro-oxigenations, is really efficient at removing by oxidation H_2S and mercaptans. Some preliminary experiments indicate that dosages of O_2 at 7 mg O_2/L/month along 6 months are required to completely remove total forms of H_2S and MeSH from red wines (*26*). Even then, MeSH will not be completely removed because it can be continuously formed if the precursor systems are particularly active. The reasons why long oxygenation periods are required, is because the complexes that H_2S and MeSH form with metals, notably with Cu^{2+}, but also with Fe^{2+} and Zn^{2+}(*20*), are in fact protecting them from the action of O_2. As it was previously commented, this mechanism is not only operative in wine, but also in environmental systems (*21, 23*). Complexed forms do not react, only the free forms do. And as most of H_2S and MeSH are complexed, the elimination of these forms by Oxygen takes quite a long time. Just tiny amounts of O_2 are really required; the O_2 taken by the wine in aeration processes such as racking is mostly wasted oxidizing wine SO_2 and wine polyphenols.

As for the role of closure, we have not been able to see large differences between closures of different permeability in regard to the wine levels of free or total mercaptans, although we have not studied periods above 1 year yet. Of course some minimum permeability is required, and all wines stored in complete anoxia accumulate free H_2S and MeSH. The good news is that closures with quite different permeabilities seem to be equally able to keep levels of free forms very low, as shown in Figure 6.

Figure 6: Effect of the permeability to O_2 of the closure on the levels of total SO_2, free H_2S and free MeSH of wines stored one year under two types of closures. Data are given as the fraction (as %) remaining in comparison to a control of the same wine stored in complete anoxia.
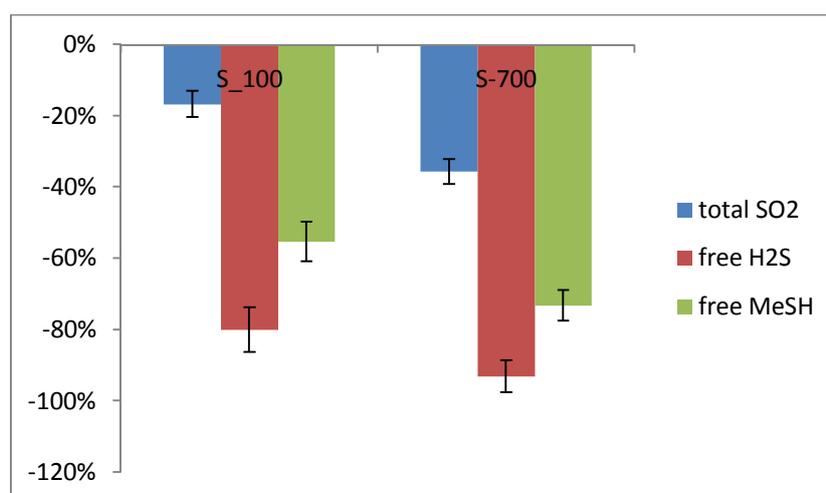
Levels of total H_2S and MeSH were not affected by the oxygen ingressed through the closure, suggesting that the O_2 permeated through the closure may be enough to keep low free levels of VSCs but not to eliminate bonded forms.

Conclusions

SH₂ and MeSH are natural by-products of fermentation and are also natural by-products of the metal-polyphenol catalyzed degradation of sulfur-amino acids. In addition, SH₂ and MeSH accumulate in wine as stable complexes with metal cations, notably with Cu(II), meaning that traditional copper finning operations do not remove, just conceal these molecules and can increase the catalytic ability of the wine to form more of these off-odors. Once the complexes are formed, aeration operations are useless for removing these compounds. Bonded forms will be slowly released when the wine is stored in anoxia, possibly because under those conditions Cu(II) is reduced to Cu°. The rate at which free molecules are released is proportional to the amount of bonded forms and inversely proportional to the copper content. The present tools most effective for dealing with this problem are prevention, extended micro-oxigenation and avoiding the use of completely tight closures. Notwithstanding this, the new understanding of the problem, the ability to make a correct diagnose of the problem and the development of analytical essays for assessing in advance the wine tendency to develop reductive off-odors will trigger the development of safer and more satisfactory solutions.

Acknowledgement

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Vincente Ferreira received the 2015 Oenoppia-SIVE award at the SIMEI trade show in Milan on 4 November 2015. The award comes with €7,500 to support research on reduction phenomena in wine carried out by his laboratory (LAAE, Laboratory of Aroma Analysis and Enology at the University of Zaragoza, Spain).

OENOPPIA is a professional association created in 2009 and grouping together the principal parties involved in the production and development of oenological products. The members of Œnoppia represent approximately 85% of oenological products used by wine makers throughout the world.

They have a strong wine culture and an international approach to the vitivinicultural world, which is expressed via the creation of this association. The groups comprising Œnoppia have for decades founded their development on research and innovation, and for the oldest, for over a hundred years. Their expertise in oenological applications is the result of internal development or long term partnerships with major universities and institutes throughout the world. They have initiated a large number of publications and patents guided by the research of the best possible expression of the potential quality of the grapes.

Marco Manfredini, president of OENOPPIA, declares: "The International OENOPPIA SIVE Award is the further concrete expression of oenological profession involvement to support innovation and general knowledge about wine".

To know more about Oenoppia: www.oenoppia.com

SIVE (Italian Society of Viticulture and Oenology) is a non-profit association of wine professionals operating in all Italian regions and companies active in the wine industry. Since 1996 promote education and professional training on wine; through its Secretariat VINIDEA, has organized more than hundred between congresses, seminars, workshops and educational tours in Italy and several other wine countries. Every two years SIVE and VINIDEA organize the event Enoforum

Since 2005, SIVE policy is to promote a better cooperation between wine producers and scientists, helping the production people to better identify their need and to formulate clear and suitable queries to researchers, and these last to prioritize their work on the topics of most usefulness for wine production.

SIVE awards were established to contribute in reaching this goal and – since 2007 to now – 236 researches participate the competition that, therefore, represents a very wide view of scientific production in the last decade, brought to the knowledge of thousands of stakeholders.

The SIVE AWARDS are granted on the basis of the judgment expressed by wine industry stakeholders.
The selection procedure foresees three phases:
the abstracts of the submitted researches will be anonymously evaluated by the SIVE Scientific Committee for the criterion "degree of innovation and interest on the topic".
the works that receive the highest scores will be orally presentation at the next Enoforum; participants attending Enoforum and the SIVE associated judge them on the basis of the criterion "benefit of research for the development of the wine industry".
SIVE Scientific Committee further judges the researches with respect to the criterion "scientific value", based not only on the summary, but on the full presentations.

Two SIVE Award has been established, each with a grant of € 7.500:
VERSINI Award since 2007, reserved to Italian researchers
OENOPPIA Award, established in 2013 and open to scientists of any country

The winner of the past editions were:
-VERSINI Award 2007: Emilio CELOTTI, Giuseppe CARCERERI de Prati and Paolo FIORINI - "Moderno approccio alla gestione della qualità delle uve rosse"
-VERSINI Award 2009: Raffaele GUZZON, Agostino CAVAZZA and Giovanni CARTURAN -"Immobilizzazione di starter malo lattici. Tecnologia, effetti biologici e fermentazioni sperimentali con ceppo di O. oeni immobilizzati in matrici ibride silice/alginato"

-VERSINI Award 2011: Matteo GATTI, S. CIVARDI, F. BERNIZZONI, S. PONI - "Effetti differenziali del diradamento dei grappoli e della defogliazione precoce su resa, composizione delle uve e qualità dei vini in Sangiovese"

-VERSINI Award 2013: Diana GAZZOLA, S. VINCENZI, A. CURIONI - "Valutazione delle capacità chiarificanti di un nuovo coadiuvante proteico estratto da vinaccioli"

-OENOPPIA Award 2013: Ramon MIRA DE ORDUÑA - "*Full automation and control of vinifications by FT-NIR spectroscopy: An innovation presenting ground-breaking opportunities*" "

The VERSINI Award 2015 was won by Fabio CHINNICI and Claudio Riponi, of the University of Bologna, with the research "Controllo dell'ossidazione di (+)-catechina mediante chitosano: ipotesi di utilizzo in vinificazioni a ridotto contenuto in solfiti"