OXYGEN ADDITIONS DURING VINIFICATION AND THE IMPACT ON WINE. 1ST PART

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Pasteur wrote in 1864, "wine is made, and matures, essentially transforming itself from a young wine to an older wine almost exclusively by the influence of air". Yet, modern enology has largely side-stepped this fundamental parameter that is oxygen for a long time.
All along the process of making the wine there is a direct influence of oxygen that relates directly to how the final wines' organoleptic profile will evolve over time.

The different contributions of oxygen

Oxygen additions are made right from the moment that the integrity of the grapes is compromised during the harvesting, and again every time, whether voluntarily of involuntarily, that the wine comes in contact with the ambient air. The contribution of oxygen is utilized by the must, by the wine and by the microorganisms that develop in the wine, notably yeast.

The utilization of oxygen in the must is essentially enzymatic and very rapid. Any measurements taken at this point are not very accurate. Therefore it is extremely delicate procedure to measure any additions and more difficult to quantify. Moutounet et al. (1) demonstrated that the quantity of oxygen consumed during the processing of the must remains inferior to the maximum capacity determined in vitro.

Yeast possess a tremendous capacity to consume oxygen, even several years after an alcoholic fermentation (2). They are therefore able to protect the wine against oxidation during the fermentation and the lees are equally effective when there is an introduction of oxygen to the wine, such as in a bâtonnage process (stirring of the lees).

In the absence of yeast in wines, the consumption of oxygen is much slower. Factors affecting the wine will depend on the wine matrix, particularly the phenolic composition and temperature of the wine. If the wine is saturated with oxygen, the literature mentions that red wines can take several days, whereas white wines can take weeks, even months for the oxygen to be consumed.

A few authors have discussed the interest of different additions of oxygen to the wine during the making of the wine (3, 4, 5, 6), but very few articles touch on the influence of these additions to the analytical and sensorial characteristics of the wine.

In the articles cited, the balance of the oxygen additions stops primarily at the bottling step, forgetting to take into consideration the gas exchange through the cork. Authors such as Kahn, Glories and Ribereau-Gayon, even confirm that the evolution of still wines in bottle are independent of the phenomenon that is oxidation (7, 8), even if their position on this topic has evolved quite a bit (9).

Indeed the amount of oxygen that can be measured in a still wine just after bottling is quite low, as it is introduced during the bottling phase and progressively consumed by the wine. Consequently the oxygen entering the bottle through the cork is also promptly consumed by the wine. Yet, the quantity of oxygen in the wine during the bottling and accessing the wine through the cork is certainly not negligible, particularly for wines with ageing potential.

Oxygen additions made at bottling and due to the exchange across the cork barrier are also responsible for the heterogeneity between a single bottling run or lot of wine. The oxygen additions done during the making of the wine (racking, filtration, cold stabilization) are all factors that homogenize the wine, whereas in the case of the bottling and cork, each bottle could have a completely different future from the rest of the lot. Each of these operations has an influence on the quantity of oxygen entering the bottle of wine, during bottling and also during the storage which will lead to a separate evolution in bottles of the same lot number. This subject will be discussed during the second part of this article.

Measuring oxygen in the tank

Up until now, analysis of oxygen was the domain of the laboratory. The first problem with this analysis was getting a representative sample from the tank and into bottle without adding too much oxygen in the transfer. The analysis needed to be done quickly.
Today, we have access to reliable equipment that can take measurements directly at the tank. Notably, these measuring devices have the quality needed for such practical applications, being robust, easy to use and calibrate with a limited maintenance- all necessary factors for being used in the cellar.
The precision of these instruments is also good, measuring to 0.01mg/L.

When is oxygen added during the course of fermentation ?
During fermentation, the wine is protected from oxygen since it is quickly consumed by the yeast and sparged by the carbon dioxide produced as well. During the course of fermentation, the use of oxygen by the wine is negligible.

The elaboration of sparkling wine allows for two opportunities to utilize the oxygen dissolved in the wine; similar to still wines, during primary fermentation, but also after bottling with the prise de mousse phase consuming available oxygen for sparkling wine.

Apart from this, oxygen additions are made at two levels :
- during dynamic process' (such as pumping, filtering and cold stabilization) or every time the wine is displaced by gravity or pumping, an oxygen transfer can occur. This is very well described by Vidal and col. (4) for each step to make wine. These articles give results for wines in the Champagne area and perfectly corroborate this author's results.
- during static phases, such as ageing in tanks, in barrels or in bottle. In this case, oxygen can get in to the wine via the openings such as tank openings or barrel hole opening, but also through the materials used : wood from barrels, crown cap weak seals and cork and synthetic cork.

Oxygen additions during wine storage and ageing

Movement with pumps
In line measurements taken during a pump-over by Vidal et al (2005) shows that during continuous operation, in a closed system, very little air is dissolved in the process. The critical steps are when the pump is turned on and shut off, where the air in the empty hoses and in the receiving tank can be dissolved in the liquid during movement.

In a comparative study of different pumps, Jean-Michel Desseigne (10) mentions that a light aeration of the must or the wine in the early transfer phase can not be avoided with alternating piston pumps or peristaltic pumps with air pockets. These results were taken in different wine estates in the Champagne wine region on tanks of several hundred hectoliters while respecting the winery's normal practice of returning the wine by the top of the tank.

The results of table 1 confirm that a pump-over returned to the bottom of the tank (no air) results in almost no oxygen addition, with a more significant contribution of air when the pump-over includes the hose returning the must or wine by the top of the tank.

Type de soutirage	Nombre d'observations	Nombre d'établissements	Apport en oxygène dissous (en mg/L)			
			Valeur min. observée	Valeur max. observée	Valeur moyenne	Fourchette moyenne
Envoi par le bas de la cuve de réception	18	7	0,05	0,51	0,25	0,12 à 0,38
Envoi par le haut de la cuve de réception	8	2	2,05	4,40	3,08	2,27 à 3,89

Table 1 : overview of the dissolved oxygen in a wine after transfer by pump-over. (First row: tank filling from the bottom; second row: tank filling from the top. Valeur moyenne = average value in mg/L dissolved O_2)

In this situation, the variations are mainly due to the height of the fall from the hose to the top of the liquid in the tank.
A measurement was taken with a pump-over returned to the top of the tank with a value of 6.5 mg/L obtained. When the wine was returned to the tank with a CIP cleaning ball, the measurement was 5.4 mg/L (only one measurement taken). Larger values were obtained (8.9 mg/L) when all the methods were used together such as aeration, rack and return with a centrifuge pump, transferred to the top of the tank.

Transport of clarified wines by truck

With tanker truck
Transport of clarified wine by tanker truck was examined between two wineries in the Champagne area. The measurements were taken on 13 compartmentalized trucks, therefore a total of 52 sections. All of the compartments were full and the distance was approximately 10 km.
For each trip the oxygen readings were taken:
- in the tank before being pumped out,
- in the tanker, after being transferred,
- in the tanker, after transportation,
- in the tank, after being pumped out of the tanker truck.

In this case, the transfer through hoses when being moved added approximately 1 mg/L, and the transport itself added only 0.1 mg/L to the wine. Therefore the transport of wine, in full containers, does not seem to add a significant amount of oxygen to the wine beside the transfer of the wine to the truck due to being pumped.

In reality the varying conditions of these wine transfers are much more significant, such as hose lengths, different pumps used, type of tanker truck, wine temperature, and total distance traveled. All these factors contribute significantly to the overall addition of oxygen to the wine. An addition of an inert gas to the hoses, the tanker, the reception tanks and reducing the speed of the transfer of wine at the beginning and end of the transfer can greatly reduce the uptake of oxygen in transported wine, as indicated by Vidal and col. (2001).

Stade	Nombre d'observations	Nombre d'établissements	Teneur en oxygène dissous (en mg/L)		
			Moyenne	Ecart type	Fourchette moyenne
Cuve de départ	52	2	0,05	0,01	0,04 à 0,06
Citerne avant transport			1,04	0,26	0,78 à 1,30
Citerne après transport			1,14	0,25	0,89 à 1,39
Cuve de réception			2,43	0,32	2,11 à 2,75

Table 2 : summary of measurements of dissolved oxygen before and after the transport of wine in tanker trucks (rows: 1=starting tank; 2=truck tank before departure; 3= track tank at arrival; 4=receiving tank)

The influence of fill levels in the tanker truck transportation of wine

Vidal and colleagues indicated that the fill level of the tanker trucks did have an influence on the oxygen uptake of the wine during transport. In fact, as soon as the compartment in the truck was being emptied, the air-wine surface exchanges increased, as did the chances of movement in the wine. In this case, the quantity of oxygen added to the wine is directly proportional to the transportation conditions, particularly the fill level of the different compartments on the truck, and the distance traveled.
The results listed in Table 3 speak volumes. The oxygen levels in some of the wines can exceed 6 mg/L due to lower fill levels in the truck during transport.

Mesure	Fourchette de valeurs en oxygène dissous (en mg/L)	Nombre d'observations
Compartiments pleins	0,35 à 1,09	6
Compartiments en vidange. 40 à 93 % de remplissage	1,20 à 6,61	7

Table 3 : summary of dissolved oxygen measurements in the tankers truck compartments in relation to their fill level.(First row: full truck tanks; second row: truck tanks with 7-60% headspace)

Clarification techniques

Different clarification techniques were tested: filtration with kieselguhr (diatomaceous earth), centrifugation and cartridge filtration.

D.E. filter
DE filtration was studied at different steps during the process; pre-filtration, filtration after clarification and after tartaric stabilization. The results are presented in Table 4. The average over 32 samples was 0.70 mg/L. DE filtration is not generally viewed as a critical addition of oxygen to the wine, but this conclusion needs to take into account the large variation in types of DE filters which can give a great heterogeneity between tanks.

As was also shown by Vidal and colleagues, it is in the clarification phase that the greatest oxygen addition is seen, mainly due to the many interstitial spaces of the product (cellulose and diatomaceous earth). Thus if several tanks are filtered through the same run of the DE filter, the first tank will have a larger oxygen addition than subsequent tanks of wine.
The last tank may also have a greater addition of oxygen due to being chased by compressed air to finish the run.

Type de filtration	Nombre d'observations	Nombre d'établissements	Apport en oxygène dissous (en mg/L)			
			Valeur min. observée	Valeur max. observée	Valeur moyenne	Fourchette moyenne
Avant stabilisation tartrique (pré-filtration ou filtration après collage)	17	4	0,15	2,02	0,63	0,07 à 1,19
Foudres après collage	3	1	0,82	1,12	0,99	0,84 à 1,14
Après stabilisation tartrique	12	4	0,10	1,79	0,72	0,15 à 1,29
Bilan général filtration	32	7	0,10	2,02	0,70	0,16 à 1,24

Table 4 : summary of results in dissolved oxygen measurements taken in the wine after D.E. filtration. (rows: 1=before cold stabilization; 2=after fining; 3=after cold stabilization; 4=general result of filtration)

The analysis demonstrates the importance of the overall volume being treated, since the oxygen uptake of 1000 hL will be very different from the result in100 hL.
Values obtained from wood tanks were higher than stainless steel tanks, probably due to stainless steel tanks being easier to empty, rather than the wine needing to be pumped out from an open door on the wooden tanks (and consequently a larger addition of oxygen related to this cellar practice).

Modular filters
Several trials were done with Modular filters (table 5).
This treatment adds a very small amount of oxygen to the wine, in the order of 0.51 mg/L.

	Nombre d'observations	Nombre d'établissements	Apport en oxygène dissous (en mg/L)			
			Valeur min. observée	Valeur moyenne	Valeur max. observée	Fourchette moyenne
Filtre à modules lenticulaires	6	2	0,14	0,51	0,75	0,33 à 0,69

Table 5: Summary of dissolved oxygen measurements with Modular filters.

Centrifugation
Centrifugation is a technique commonly used in the Champagne area, and on important quantities of wine. A series of trials was done in six wineries and the results are shown in table 6.
As for the filtration, the average over these trials following a centrifugation treatment was not very significant with 0.95 mg/L.
One can observe that some wineries use centrifugation and filling a tank from the top, which leads to higher rates of oxygen absorption (this is done more from a practicality level than by necessity.

Type de remplissage après centrifugation	Nombre d'observations	Nombre d'établissements	Apport en oxygène dissous (en mg/L)			
			Valeur min. observée	Valeur max. observée	Valeur moyenne	Fourchette moyenne
Renvoi par le bas ou tuyau plongeant	19	6	0,08	2,85	0,95	0,26 à 1,62
Renvoi par le haut	4	1	2,55	2,81	2,67	2,55 à 2,79

Table 6: dissolved oxygen readings in wine after centrifugation.
(First row: tank filling after centrifugation from the bottom; second row: from the top)

Tartaric stabilization

Continuous tartaric stabilization

The emphasis in this trial was placed on continuous flow cold stability since any other techniques are no different from the ones already mentioned above. For example, cold stabilization is a process of pumping the wine, storing it and racking and filtering again. An essential point to consider is the temperature effect on the absorption of oxygen which is much more significant at cooler temperatures, and requires much more careful handling of the wine.
The measurements for this trial of continuous flow cold stabilization were done in the tank before the treatment, and again in the tank after the treatment (table 7).

The average result for the wines in this treatment was an oxygen addition of 1.22 mg/L. This value is slightly higher than the measurement for D.E. filtration.
The tartrate crystallization process does not seem to have a significant impact of the uptake of oxygen. There are some wide variations in the results, most likely due to the filtration.

	Nombre d'observations	Nombre d'établissements	Apport en oxygène dissous (en mg/L)			
			Valeur min. observée	Valeur max. observée	Valeur moyenne	Fourchette moyenne
Passage au froid en continu	17	3	0,09	2,58	1,22	0,58 à 1,86

Table 7: Summary of the dissolved oxygen measured after a continuous cold stabilization treatment

Comments

Firstly, it was interesting for us to compare our results with those found in the bibliography. The first observation was that there are very few specific values in the literature. Moreover the numbers mentioned do not hold up to details regarding materials used (if mentioned at all) and the amount of repetitions done in a given trial. Table 8 summarizes the values we were able to collect.
The most complete study was the one often quoted by J.-C. Vidal and the team of Mr. Moutounet. Their thoroughness in the many different possibilities of oxygen additions allowed for a better understanding of the exact mechanics of these additions and their effect on the wine. These results allow simple and practical solutions to be applied to current practices, when the objective is to reduce the amount of oxygen introduced during vinification.

In the Champagne are, previous to this study, only the work of D. Mariotti at Moët & Chandon was available. The values obtained from the CIVC are, with the exception of the tartaric stabilization, in agreement with those of Vidal, of Mariotti and even with Ferrarini's Italian group.
The values obtained by Vivas and Glories are on all levels much higher than those observed by the other authors. It should be mentioned that these results were obtained with different equipment.

Etapes	VIVAS et GLORIES (1996)		FERRARINI et col. (2001)		VIDAL et col. (2001)		MARIOTTI (1999)		VALADE et col. (2005)	
	Valeur moyenne (en mg/L)	Commentaires	Valeur moyenne (en mg/L)	Commentaires	Valeur moyenne (en mg/L)	Commentaires	Valeur moyenne (en mg/L)	Commentaires	Valeur moyenne (en mg/L)	Commentaires
Soutirage par le bas de cuve	3,0	Pas d'indication sur la méthode et sur le nombre de répétitions	0,7	26 répétitions	0,1 à 0,2	12 répétitions	0,1	12 cuves dans une	0,3	18 répétitions
Soutirage par le haut de cuve	6,5		1,0	20 répétitions	/	/	/	/	3,1	8 répétitions
Filtration sur terre	6,5		0,7	26 répétitions	0,7	6 répétitions	2,4	Pas de répétition	0,7	32 répétitions
Centrifugation	7,5		2,3	14 répétitions	0,9	Pas de répétition	0,2 à 0,7	3 répétitions	0,9	19 répétitions
Stabilisation tartrique en continue	/	/	5,6	7 répétitions	2,4	3 répétitions	1,5	Pas de répétition	1,2	17 répétitions
Transport en citerne	/	/	/	/	0,4 à 3,3	4 valeurs fonction du niveau de remplissage	/	/	0,1 à 6,6	65 valeurs fonction du niveau de remplissage

Table 8: synthesis of the literature results of oxygen absorption in various enological cellar practices (Rows: 1=racking / tank bottom; 2=racking / tank top; 3=kieselgurh filtration; 4=centrifugation; 5= continuous cold stabilization; 6=tanker truck transport)

From these values, it is possible to estimate the quantity of oxygen that a wine is exposed to during common cellar practices. In the early phases while there is still yeast present, one can consider that there is very little contribution from either racking or transfers due to the small addition balanced with the

yeast actively scavenging any available oxygen. The most significant additions are therefore made pre-clarification and post-malolactic fermentation up until the bottling phase. During these various phases in the production of wine, it seems the absorption of oxygen is quite small when one considers that in the trials no precautionary additions of inert gas were used.
To add emphasis to the results, the methods practiced in the three different winery operations were similar in function and added to the validity of the results.

Overall additions on the three different trials are respectively from 3.9- 4.4 and 4.5 mg/L. During these 3 trials, the wines experienced a centrifugation and returned to the tank by the top, which accentuates an addition of approximately 1.5mg/L.
The addition of oxygen during normal cellar operations right up to bottling can be estimated at 3 to 5 mg/L (not considering some of the specific practices mentioned in the article). It is important to remember that these values could be different for smaller lots of wine, than for larger ones.

Certainly, when observing good fermentation and winemaking throughout vinification, the overall addition of oxygen is very small compared to possible 'bad winemaking' practices.
As was very well demonstrated by Vidal and colleagues, these excess oxygen additions are found in moving the wine through long hoses, starting up and stopping pumps, filling a tank from the top, not filling tanks to the top during transportation and not chasing the wine with an inert gas during clarification procedures (centrifugation, diatomaceous earth).
An assessment needs to be done for each winery to determine which practices are sources of oxygen introduction to the wine during production and storage.

Simple corrective measures can be done to limit the aeration of the wine by using inert gas in the hoses during the transfer of wine, filling a tank from the bottom, and transporting the wine in full containers. If, despite precautionary methods, there is still an important addition of oxygen (greater than 1mg/L in white wines, for example) it is still possible to sparge the wine with nitrogen while moving the wine.

In this study, we did not touch on the subject of wine aged in barrels, still a marginal practice in the Champagne area.
This type of vinification is definitely more oxidative, even if it was just considering the small volumes involved, but also the permeability of the material: wood.
The experimental design used to assess the amount of oxygen in barrels is quite complex and difficult. These trials need a great deal of rigorous testing since there are so many parameters to be considered in a barrel: the size of the barrel, the age, the origin of the wood, the toast level. The numbers mentioned in the literature are in the range of 10-45 mg/L according to Vivas N. and Glories Y.

The effects of bâtonnage (stirring the lees) have been measured. As one might expect, since the stirring of the lees means putting the yeast back in suspension and therefore contributing to utilizing any addition of oxygen, a classic bâtonnage does not add any oxygen to the wine overall.

Conclusion

Oxygen additions made to the wine during well-regulated winery operations are in the order of 3 to 5 mg/L.

In reality, and sometimes accidentally, these additions can easily jump to being two or even three times as high in extreme cases.
The real question behind all these trials boils down to; how much oxygen does a wine need to reach its maximum potential, without surpassing this ideal number? The answer is far from being easy, or universal. It will always be difficult to assess as many factors, such as the origin of the wine, cellar conditions and winemaking practices, length of storage before being consumed and the style that the winemaker intends the wine to have.

If we agree that the effects of oxygen are cumulative, then each addition has an effect on reaching that maximum potential, with tremendous differences between different wine, if even just considering whites, rosés and reds.

One must also consider the sensorial impact of oxygen on the wine, which is no less obvious a contribution than the steps described in the article.

For still wines with great ageability and also sparkling wines, oxygen additions in the bottling phase are very important. Another aspect that separates oxygen additions during vinification in tanks vs. in bottles is the heterogeneity and homogeneity and their effects on the wine. A tank volume of wine can be considered quite homogenous before the bottling phase, no matter what the wine making processes it has gone through up until then. At the bottling phase, oxygen can affect each bottle differently, depending on the cork and other small factors contributing to this heterogeneity on a bottle basis, even within a particular lot. These aspects will be written about in greater detail in the second part of this article.

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