DISSOLVED OXYGEN MEASUREMENT: A NEW STANDARD FOR QUALITY CONTROL?

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INTRODUCTION

In general, the presence of oxygen is potentially linked to wine alterations.
In wine, oxidation depends on the oxygen concentration and on the time of enrichment.
In general in enology, a forced oxidation is more unfavorable than a slow and continous dissolution of oxygen that usually plays a positive role on the wine evolution.
The relationship between the oxygen and the grape must, the oxygen and the fermentation, and between the oxygen and the wine can't be considered in the same way, because the mechanisms involved in the oxygen consumption are different.
On the other hand, the exchanges of oxygen between these different media are all governed by the same gas law.
This presentation is focused only on the status of the oxygen dissolved into the wine in order to question on the interest and on the expected consequences of the measure of dissolved oxygen during the process of making wine.

-MEASUREMENT OF THE OXYGEN IN THE CHAI: WHAT THE BASIS?

Oxygen solubility
The air is a mixture of nitrogen and oxygen, for the higher parte, and other gas present in small proportion. The gas exchanges between wine and air are governed by the partial pressure equilibrium. The oxygen in the air represents about one fifth of the volume. In normal conditions, its partial pressure is at 1013 hPa, 20°C, and in respect to the air saturated with water vapor, 206 hPa. In these conditions, at the saturation equilibrium with respect to the air, the wines incorporate 6 ml/l or 8.4 mg/L of dissolved oxygen.
In constant pressure condition, the concentration dissolved oxygen decreases exponentially with the increase of temperature, whereas it increases proportionally with the pressure. The oxygen as well as the nitrogen are gas with low solubility if compared to carbon dioxide, for instance.

Oxygen Dissolution
When a gas comes in contact with a liquid phase, it will tend to diffusing into it progressively; the maximum that can be reached corresponds to the saturation level for a defined pressure and temperature. The dissolving rate is described by the diffusion law , and it is essentially dependent on the surface of contact gaz/liquid (m^2/m^3). Then the rate of enrichment of the wine in oxygen from the air is increasing with the increase of the surface of the liquid phase and with the increase of the finesses and persistence of its emulsion with the air. To a lesser extent, low temperature is also a factor promoting the rate of diffusion. After its dissolution, the presence of oxygen in the wine is not stable during the time. The dissolved oxygen is progressively consumed by different substrates.

Oxygen consumption
In a wine saturated with air, the oxygen consumption occurs in a time of one to several weeks. The kinetic of consumption is faster for the red wine than for the white one. The rate of consumption of the dissolved oxygen by wine highly depends on the temperature. In enology conditions, the oxidation kinetics are very slow if compared to the enzymatic oxidation occurring in the grape juice.

If the air is renewed, the oxygen consumption will carry on. The total absorption capability of the wine is very high; it is about 80 mg/L for the white wine and 800 mg/L in the red one. Therefore, the consumption capability out of proportion to the possibility of dissolution throughout several processing the wine undergo to, since the consumption of 800 mg/L equals the effect of near one hundreds racking.

The oxygen dissolved into the wine

The amount of dissolved oxygen present at a certain time depends on the kinetic of dissolution and on the kinetic of consumption; the temperature plays a rule inverse on this rate. In general, when the wine mass is agitated (pumping, decanting, racking, "batonnage"…) the kinetic of dissolution the oxygen from air in contact of the wine is higher than the oxygen consumption from the wine components; in this condition we can measure amount of dissolved oxygen in the order of mg/L, and the saturation can be reached in function of the vine surface offered to the air. The oxygen dissolved during several wine treatment reacts with the wine components and progressively disappears in the medium until reaches very low values (tens µg/L). As a result, in a static regime (wine stored in tank, aging, and partially also in the case of bottled wine) the kinetic of dissolution become lower than the one of consumption in such a way that in the wine the concentration of dissolved oxygen became very low (in the range of 10-40 µg/L). In this case if the wine surface is in contact with a gas phase that contains a portion of oxygen, there is a very thin zone that will be in equilibrium of saturation with the gas phase considered and is establishing a gradient of concentration in oxygen on the wine surface (Moutounet et Mazauric 2001).

- OXYGEN NMEASUREMENT IN THE CELLAR: ANY COMMENTS?

The measurement of dissolved oxygen in the wine should be adaptable to the different enological conditions previously mentioned, and this requires instruments with different sensitivity. It is necessary to be able to measure ppm as well as ppb. Moreover, this measurement it should be done on site. This discriminate the measurement of oxygen dissolved from other analytical measurement currently used for the wine analytical testing on a sample taken from the mass. In optimal conditions, the evaluation of the oxygen enrichment caused by specific wine making process, needs a specific instrument able to take a measurement at the beginning and at the end of the equipment tested, at the entrance and at the exit of the wine flow simultaneously.

The first data used by Ribéreau-Gayon (1931) have been carried out by chemical analysis. The test was based on the oxidation of sodium hydrosulfite by the oxygen in presence of the redox indicator indigo carmine. After the work of Clark (1956) the use of polarographic probe was diffused for measuring the oxygen dissolved in water, and in beverages…essentially because of their easiness. The significant improvement of the technology producing polarographic probe and the development of the Hersh galvanic cell to measure micro amount of oxygen in the nuclear industry, made available instruments able to measure microliters of oxygen per liter. These techniques opened new way to interpret oxidation phenomena in the wine (Moutonet et Mazauric 2001). Since not so long ago, a new generation of equipment using luminescence as assya principle appeared. Among these different possibility, the technical choice is mostly guided by the required level of precision of the results; instrument for measurement limited to 0.1-0.2 ml/L, and instruments that allow to measure µL/L are available. Investment costs and easiness of calibration and maintenance are also taken into account. For very low concentrations drastic precaution has to be adopted in the method set up (Moutounet et Mazauric 1999).

- WHAT IS THE BALANCE OF THE OXYGEN MEASUREMENT IN THE CELLAR

From the moment the wine is moved and gets in contact with the wine it become susceptible to dissolve oxygen. Several surveys have monitored the amount of oxygen dissolved in the barrel storage area, and in the bottling zone of the winery collecting data on the degree of enrichment and its variability in enological conditions; In relation to each specific operation (filtration, centrifugation...) the amount of dissolved oxygen is strictly dependent on the way the different equipment is used. The enrichment occurs mainly at the beginning of the mass transfer if the circuit, if not saturated with inert gas. It also occurs at the end of the process in the case no particular control precaution is taken at the end of the operation (Vidal et al. 2001). In these different situations, the global enrichment occurring at the exit depends essentially on the processed volume penalizing the over sized equipment along with little volumes. Data collected in continuo

during centrifugation showed that the oxygen is dissolved on a regular basis at the time of each evacuation of the sediment collected in the centrifuge basin; operating such device under nitrogen atmosphere should allow to mitigate this enrichment to hundreds microliters per liter (Vidal et al. 2003). The comparison of test in several location shows that filtration (perpendicular or cross-flow) could lead to oxygen enrichment from 0.1 to 2.2 mg/L, whereas tartaric stabilization is at the origin of a more higher enrichment (from 0.6 to 5.7 verified). Bottling is one more critical point for potential enrichment in oxygen, so well identified that manufacturers are offering several solutions more or less sophisticated, highlighting that the problem is not of easy solution (Vidal et al.2004 a). Furthermore, our measurements are showing the importance of the head space as source of oxygen for the wine after the closure (cork, screw cap....or "Bag in box" valve) is positioned (Vidal et al. 2004b).
The existence of several occasions in which the oxygen can get dissolved in the wine before bottling explains why it is not rare to find in the bottled wine amount of dissolved oxygen in range from 2 to 4 mg/L. On the other hand, it is also possible to find wine on their way out from the bottling line with dissolved oxygen close to 0.3 mg/L. The effort put in the bottling operation management can be annulled by the presence of wine already rich in dissolved oxygen because of defective wine transfer operations.

-MEASURING OXYGEN IN A CELLAR: WHY?

The global situation described above it is well known since the first studies from Ribéreau-Gayon (1961); these data are based on the basic notion and the proposed solutions are most of the time a matter of common sense after the phenomena regulating the gas exchange between the liquid phase and the gas became known. Why it is still topical then? At a first analysis, it seems to be related to several reasons in conjunction. Sine long ago sulfite has been abused in winemaking in order to prevent wine oxidation. The knowledge acquired in this practice has been faced sensory defects due to excessive addition and the increasing consumer disaffection for those products with too much sulfite. The tendency is to decrease the addition of sulfite into the wine, in such a way that in the sensory evaluation carried out by official panels the description of wine "very oxidized" or "too much oxidized" have been observed with increasing frequency. In the meantime a higher request from the market of wine with dominant fruity character has been observed. In relation to the commercial circuit, such character last for a relatively short time. Precisely, taking into account the chemical reactivity of the molecules involved in this sensory characters, the diminishing of the aromatic potential is most likely due to phenomena of oxidation. Then it has been attributed to unacceptable amount of dissolved oxygen in the wine at the time of bottling. Moreover, the average increase of wine pH over successive vintage emphasized the phenomena described above. In fact, at high pH the fraction of sufites active against oxidation decreases and the oxidation rate involving polyphenols increases. Therefore the importer, in particular the one from the country that do not produce wine, have new demand for the market.
This analysis mostly based on macroscopic indicator does not claim to be complete and arises from the need to consider the presence of oxygen dissolved into the wine; in fact if the hope is to put on the market wine that are potentially sensitive to oxidation and with low amount of sulfites it is necessary to avoid the presence of dissolved oxygen. In order to solve this simple equation in the winemaking practice, it appeared necessary in a first instance to evaluate the critical point of oxygen enrichment on the all wine processing chain from the reception to the bottling. Available instruments and their adaptation to the bottling line have been developed and is technically operational. Beyond these observations, it is clear that it is necessary the availability form the industry to invest and to adopt this quality approach. Some winery has chosen to adopt a deoxygenating plant, even if the industrial technique available has some several inconvenient. In consequence of these different approaches, it is necessary to a control system proper for quality assurance this analytical criteria. On-line measurement of dissolved oxygen, object of some realization from different branches of the beverage industry, would assure the good functioning of the used equipment and complete the tracking criteria of lots introduced in the market; here it is the interest and the mayor aim of the oxygen measurement in the cellar. The measurement on collected samples should not became prescriptive in the commercial exchanges, because this analysis it is not representative a posteriori, the oxygen will be consumed, the analysis will depend on the temperature and the length of storage of the samples. In addition, who knows the admissible quantity of oxygen for the bottled wine…? Is there only one value? Is there an optimal quantity in relation to the wine typology or to the targeted

market? Nowadays the research does not have yet the instrument to be able to answer to these questions with scientific arguments. In fact the problem is so complex and difficult to approach that the conclusion can't be applied in a general way. However, it seems that for a certain number of rosé wines and for the white dominated by aromas of the kind "varietal thiols", it is necessary to put in action all the available technique in order to avoid the enrichment in oxygen. On the opposite side, the "structured" red wines in particular, are less exigent in the matter of amount of oxygen at bottling such as the wine that develop their "bouquet" after a long aging in bottle.

CONCLUSION

Setting up of the measurement of the oxygen dissolved in the winemaking process is a innovative project well integrated in the quality assurance context for a wineries; Such involvement will preserve at the best the qualities acquired during the winemaking process and the aging, and will promote the conquer of the international market.

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Références bibliographiques

-Moutounet M., Mazauric J.P. 1999- Dosage de micro-quantités d'oxygène dans les vins. Feuillets Verts de l'OIV, n°1085.
-Moutounet M., Mazauric J.P.- 2001- L'oxygène dissous dans les vins. Revue française d'œnologie n° 186, 12-15.
-Ribéreau-Gayon J. – Oxydations et réductions dans les vins. Thèse Ed. Delmas Bordeaux, 1931.
-Ribéreau-Gayon J., Peynaud E. -Traité d'œnologie, Tome II, 1961.
-Singleton V.L. -Am. J. Enol. Vitic. 1987, 38, 69-77.
-Vidal J.C., Dufourcq T., Boulet J.C., Moutounet M. 2001- Les apports d'oxygène au cours du traitement des vins. Bilan des observations sur site 1ère partie. Revue française d'œnologie n° 190, 24-51.
-Vidal J.C., Boulet J.C., Moutounet M. 2003- Les apports d'oxygène au cours du traitement des vins. Bilan des observations sur site 2ème partie. Revue française d'œnologie n° 201, 32-38.
-Vidal J.C., Boulet J.C., Moutounet M. 2004 a- Les apports d'oxygène au cours du traitement des vins. Bilan des observations sur site 3ème partie. Revue française d'œnologie n° 205, 25-33.
-Vidal J.C., Toitot C., Boulet J.C., Moutounet M. 2004 b- Comparison of methods for measuring oxygen in t