PANORAMA

OXYGEN INGRESS DURING AGEING

SEGUIN MOREAU / R & D department: oeno@seguin-moreau.fr

WHAT IS THE ROLE OF OXYGEN DURING AGEING?

Ageing in wooden barrels is an essential step in the production of quality wines. At the end of the ageing process, wines aged in wooden barrels have organoleptic qualities reflecting both the complexity and originality that create their personality. Two physico-chemical processes contribute to achieving this evolution in wine: the solubilization of volatile and non-volatile compounds contained in the wood, concomitant with the dissolution of oxygen in the air into wine. Oak wood is a porous material permeable to gas. This enables exchanges to occur with the surrounding air throughout the ageing process.

Air is composed of 21% oxygen. It is involved in many chemical or biochemical reactions that cause changes in inert and living matter. It is a sort of motor for many processes, which are described as oxidizing when oxygen is present and reducing when it is absent. In normal conditions most commonly found in wine cellars, oxygen is also involved in every step of wine production. Oxygen and oxidizing processes may either help or harm the evolution of wine, depending on how well its ingress is controlled. It is important to evaluate these processes.

HOW DOES OXYGEN INGRESS OCCUR DURING AGEING?

It is generally agreed that oxygen transfer from the air into wine can occur in two ways:

- **during ageing in hermetically sealed wooden barrels (with a silicon bung, hammered-in bung)**
- **from handling the wine (by opening the bung, racking, etc.)**

There is thus a distinction between the slow and gradual ingress of oxygen by ageing in wooden barrels and what may be a sudden transfer during racking operations.
Oxygen content due to racking or ullage is very variable and depends on how carefully these procedures are carried out: the oenological literature mentions **dissolved oxygen contents ranging from 0.1mg/L to over 5-6mg/L during racking.**

Conversely, given the complex nature of the processes brought into play, evaluating the concentrations of oxygen ingress during ageing in wooden barrels is still a source of investigation. The first person to address this field of research was Ribéreau-Gayon in 1931: using a rudimentary, permanent ullage procedure with a sulfur dioxide solution, he established that only limited transfer of oxygen from the air occurred through the wood; between 2 and 5 ml of oxygen per liter per year. On the other hand, **oxygen penetration into hermetically sealed wooden barrels was around 15 to 20ml/L/year.** In other words, the actual quantities of oxygen observed could not be explained by merely passive wine-atmosphere contact via the wood.

Almost 60 years later, this research was taken up again by Vivas (Bordeaux) and Feuillat (Dijon), and then Moutounet (Montpellier), although they focused their attention on other aspects of this issue. The origin and anatomical structure (grain, density, etc.) of the wood have a major impact on the kinetics of oxygen transfer through the staves. When the wood becomes saturated with wine (in reused barrels), oxygen dissolution slows down. The hermeticity of the bung also plays a major role.

HOW DOES OXYGEN SOLUBILIZE IN WINE AGED IN WOODEN BARRELS?

To answer this question, two physical processes must be distinguished, which first enable oxygen to penetrate into the wooden barrels and then solubilize in the wine.

How does oxygen in the air enter inside a hermetically sealed wooden barrel?

When air ingress through the bung hole is restricted, a depression is created inside the barrel that may reach a level of over 120 mbar. This depression occurs when the loss in volume from wine absorption by the wood or evaporation during ageing is not directly compensated by air ingress. For this reason, sudden air ingress into the headspace of the barrel always occurs when the bung is opened. The more intense the evaporation loss (the "Angels' share") and the longer the intervals between ullages, the greater the depression. In some cases, this causes the wooden barrels to lose hermeticity.

Various mechanisms compensate for this depression:

- wine degassing: elimination of CO2 produced during fermentation
- air penetration through wine-saturated wood: via the staves or head pieces, as well as joint parts (gaps and croze)
- air penetration through dry wood in the non-wine-saturated section (headspace)
- micro-warping of heads: warping or slight movement creating preferred passage routes for oxygen contained in the air.

For this reason, it is often recommended to carry out regular ullage of the barrels. Evaporation loss (the "Angels' share") can be considerably lowered by controlling the hygrometry (80% HR) and temperature (<18°C) of the wine cellar. By way of information, the average rate of evaporation loss (the "Angels' share") measured during ageing in new barrels for 10 months in a wine cellar is 1-6% per year.

.../...

Oxygen that penetrates inside the barrel is either consumed by the wine or found in the headspace, thus balancing the "evaporation / depression / mechanical stresses" system. It has, however, been proved that the headspace is highly depleted in oxygen (containing 0-5% oxygen), which shows that wine consumes oxygen very quickly. Opening the bung hole introduces oxygen into the headspace. This oxygen must then be 'driven out' quickly when the barrel is filled up (ullage).

How does oxygen dissolve in wine?

Generally speaking, the kinetics of oxygen dissolution depend on its concentration in the liquid and gas phase, the surface area for exchange between these two phases, the nature of the liquid (its ethanol level, for example) and the temperature. By changing these parameters, as well as the contact time between the wine and oxygen, the dissolution of oxygen in wine can be influenced.

Methods for restricting wine/oxygen contact, and hence oxygen dissolution during transfer operations, are well known and the following examples may be cited:

- checking seals and connections for airtightness
- paying attention to the presence of emulsion
- using inert gases (carbon dioxide and nitrogen, singly or as a mixture) before filling the barrels.

HOW DOES WINE REACT WITH OXYGEN?

Oxygen dissolves in wine and is then gradually consumed. It is therefore not a stable component for wines. The main substrates resulting from oxidation are phenolic compounds, which are responsible for consuming dissolved oxygen. The reaction pathways involved are extremely complicated, however, and much remains a matter of speculation.

The speed at which dissolved oxygen is consumed depends on the type of wine. For example, red wine requires an average of 96 hours and white wine an average of 15 days to consume 8mg/L of dissolved oxygen. These figures are given as indications since the speed at which dissolved oxygen is consumed increases as the temperature rises.

The other components of wine involved in oxidation reactions are metal cations, yeast lees, sulfur dioxide and ethanol. These compounds include oxidation catalysts, antioxidants and substrates involved in oxidation mechanisms. When wine takes up oxygen, it thus accumulates intermediary oxidants. These forms act directly on the delicate aromatic components of wine.

Lees present during ageing in wooden barrels, which applies always to most white wines and often to red wines, play a major role in the kinetics of oxygen consumption. It has been proved that lees consume oxygen faster than wine components, thereby protecting the wine from oxidation. Re-suspending the lees by stirring at regular intervals helps their activity. Nevertheless, care is needed regarding oxygen ingress caused by the opening of barrels during this operation.

TO SUMMARIZE, WHAT ARE THE MAIN FACTORS AFFECTING OXYGEN TRANSFER INTO WINE?

The following are the main factors influencing oxygen dissolution in wine during ageing in wooden barrels:

- age and mechanical properties of the barrel
- anatomy of the wood
- frequency of racking
- use of inert gases
- frequency of ullage
- choice of bung
- temperature and hygrometry control in the wine cellar.

WHAT ARE THE EFFECTS OF OXYGEN DISSOLUTION IN WINE?

As mentioned previously, there may be positive or negative effects. The positive effects include the elimination of 'reduced' aromas arising from yeast metabolism, color evolution in red wines, the involvement of oxygen in reactions with wine tannins and lower astringency.
Nevertheless, when too much oxygen is present it may harm the quality of wines during ageing. Oxygen causes chemical processes expressed first by a loss of fruity aromas in young wine and their replacement by heavier sensations reminiscent of honey and wax in white wines, and prunes and figs in red wines. This irreversible change in wine aroma is always accompanied by a color change: red wines turn to shades of orange, and white wines acquire yellow/honey-colored hues.

Oxygen ingress is therefore only beneficial if it is strictly controlled and monitored. Wine tasting remains an essential tool for monitoring the correct evolution of wines and their possible oxygen requirements.

HOW IS THE PRESENCE OF OXYGEN IN WINE MEASURED? WHAT IS REALLY MEASURED?

Given the importance of oxygen dissolution and consumption processes, it is important to specify that devices measure only the parameter of 'dissolved oxygen' content. Oxygen already consumed is not included in this level.

There is currently no method for directly measuring the amount of oxygen consumed. This can be done by evaluating total oxygen ingress during the wine's lifespan, although this obviously remains a rough figure.
Another approach is to monitor chemical markers. This involves monitoring the concentration of chemicals produced or degraded by oxidation. **The concentrations of these compounds enable the presence of dissolved oxygen and the oxidizing processes that follow, to be evaluated. The classic example of such a marker is SO2.**

.../...

WHAT ARE THE MEASURING DEVICES?

Two techniques for analysing dissolved oxygen are currently available. They are based on electrochemical or optical measurements. Most of the oxygen electrodes (optical sensors) currently available on the market are designed and adapted to the inherent constraints of use in wine cellars and under wine-making conditions.

Technical features of several sensors used in wine cellars and oenological laboratories:

Principle	ELECTROCHEMICAL		OPTICAL	
Model	TriOxmatic 700IQ	Orbisphere 311	LDO HQ30	Presens PSt3
Quantification Limit	0 à 20 mg/L	0,0001 à 20 mg/L	0 à 20 mg/L	0 à 45 mg/L
Trace Measurements	NO	YES	NO	YES
Interference	CO2	LOW	NO	NO
Stirring at Membrane level	YES	YES	NO	NO
Comments	Take care to maintain the sensor	Strong and highly sensitive	Adapted for use in wine cellars	Non-invasive measurement
Price indication (Euros)	< 1000	> 10 000	> 1000	> 10 000

TriOxmatic and LDO HQ30 sensors are found mainly in wineries. The other two sensors tend to be reserved for laboratory use.
One benefit of the LDO HQ30 optical sensor is that it automatically corrects measurements according to the temperature, pressure and salinity of the environment. Furthermore, unlike traditional electrochemical methods, no calibration is required and measurement does not consume O2, meaning that no stirring is required. In addition, sensor components do not clog up and are hence not prone to drift.

WHAT RESEARCH IS IN PROGRESS?

In collaboration with Bordeaux's Faculty of Oenology, our research team has been working on the theme of premature ageing in red wines. **For the first time, we have identified an olfactory marker of oxidation-induced evolution of red wines. This is the result of several years of research. It is a diketone: 3-methyl-2,4-nonanedione**, whose aroma is reminiscent of prune stones.

Much research is in progress to evaluate the effect of wine ageing methods on the formation of this compound. The search for its precursors is also a priority. Understanding a marker of oxidation-induced evolution of red wines should shortly enable us to progress in understanding the physico-chemical factors governing the suitability of red wines for ageing.

GOING A STEP FURTHER

« Oxygène et Vins : du rôle de l'oxygène à la technique de micro-oxygénation » de A. B. Bartolini, Parsec Editions, 2008.

« L'élevage des vins », numéro hors série du Journal International des Sciences de la Vigne et du Vin, 2002.

« L'oxygène dissous dans les vins » de M. Moutounet et J.P. Mazauric, 2001, Revue Française d'Oenologie n° 186, pages 12-15.

BIBLIOGRAPHY

1. Feuillat F., Perrin J.R., Keller R., 1994 Simulation expérimentale de « l'interface tonneau ». Mesure des cinétiques d'imprégnation du liquide dans le bois et d'évaporation de surface. Journal International des Sciences de la Vigne et du Vin, 28, 3, 227-245.

2. Moutounet M., Mazuric J.P., Saint-Pierre B., Hanocq J.F., 1998, Echanges gazeux des vins logés en barriques. J. Sci. Tech. Tonnellerie, 4, 115-129.

3. Ribéreau-Gayon J., 1931, Contribution à l'étude des oxydations et réductions dans les vins. Thèse, Université de Bordeaux.

4. Vivas N., Debeda H., Menil F., Vivas de Gaulejac N., Nonier M.-F., 2003, Mise en évidence du passage de l'oxygène à travers les douelles constituant les barriques par l'utilisation d'un dispositif original de mesure de porosité du bois. Premiers résultats. Sci. Alim., 23, 655-678.