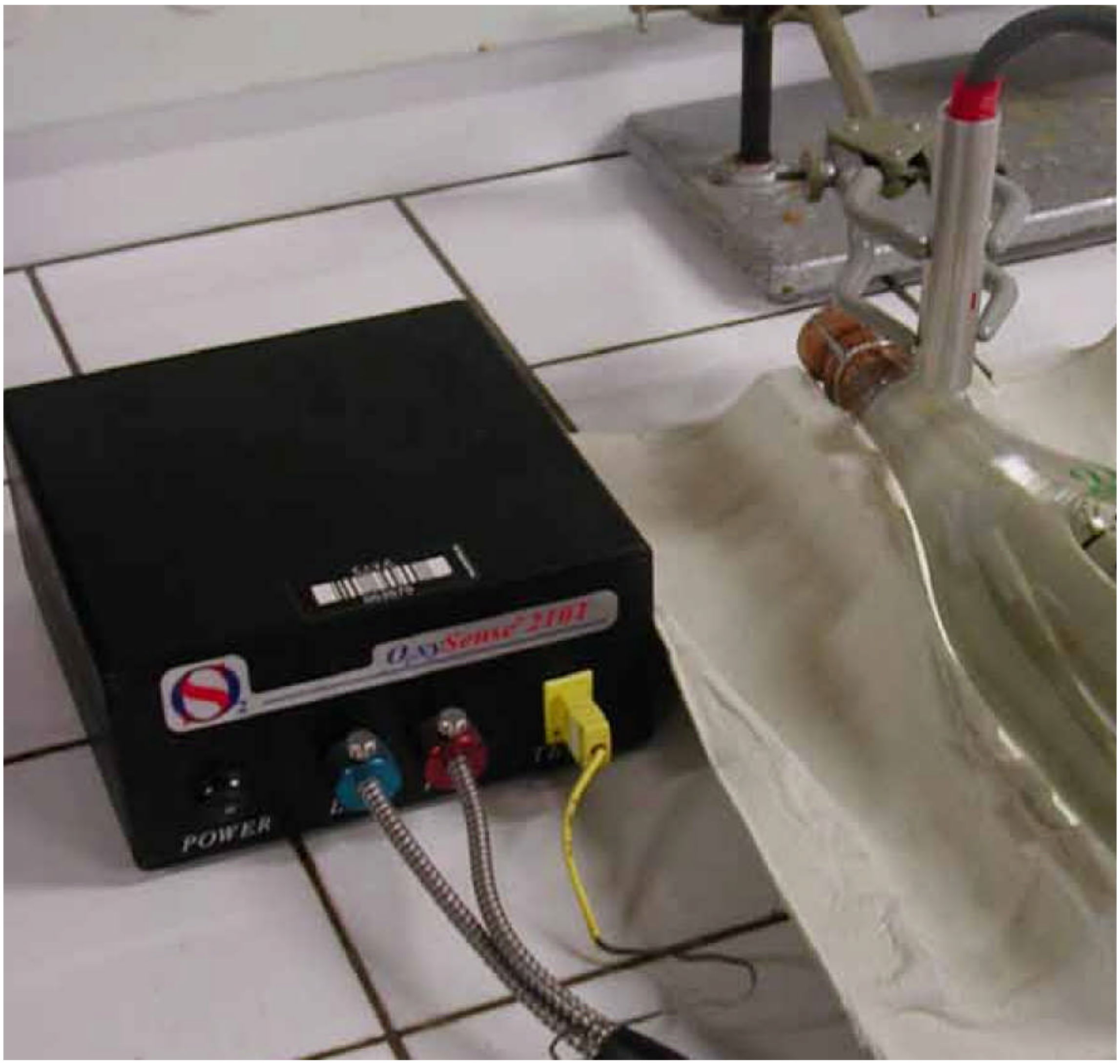
Wine

Measuring Oxygen In Bottles by Chimilunescence



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The difficulty in measuring oxygen has long been an obstacle to the studies for its effects on wines.

Only since the 90s, with the development of the first portable tests (oximeters), has the wine world gradually become interested in oxygen's role in winemaking, and more recently, it effect after bottling and corking (1).

Just looking at the number of articles about oxygen, confirms that there is a real and growing interest in the subject in the wine world.

The subject of oxygen and its effect on the aging of the wines is not new in Champagne. Since the end of the 80's, the professionals in Champagne are aware of the importance of the choices of the capsules. . Our work has shown that the micro-quantity of oxygen that penetrates through closures contributes to the sensorial evolution of the champagnes (2,3,4,5).

The Wine

Every year, from the results of the Laboratory National d"Essais (LNE)), we publish the characteristics of the different caps marketed in terms of then gaseous changes. This information helps of the winemaker make his choice of the closure to be used based on the composition and commercial destination of each of its wines.

But these measures are complex and limited by the accuracy of the instruments.
We measure the gas output in 1/10 of centimeters in 24 hours for the carbonic gas in a 100th of centimeters in 24 hours for the oxygen.

Since the general assembly of the AVC, we have sought to a method to achieved these studies from inside the bottle. This technique exists presently through the use of hemiluminessence. The principle, which will be detailed later, consists of sending a luminous beam through a clear bottle towards a pastille glued to the glass in the bottle's interior. The light reflected by the pastille is proportional to the quantity of oxygen in its proximity. This allows quantifying the amounts of oxygen after corking.

It also permits thew measurement of the oxygen's consumption in bottled wine. However, we will limit this article to measure the amounts of oxygen at the time of corking, the actual corking.

Measuring Oxygen Dissolved In The Wine.

Until recently, the method used to measure oxygen in a bottle has always been destructive. , These tests provided a value at a certain point in time, but did not allo follow up on the accumulation or consumption of oxygen by the wine in the same bottle over time.

In 2005, Paulo Lopez proposed a non destructive colorimetric method for measuring dissolved oxygen in water, based on the work of Ribereau Gayon (7-8). This method is based on the use of a colored indicator, the carmine indigo. This yellow dye gradually turns blue when in contact with oxygen. It permits the monitoring of the accumulation of oxygen over time. But this method has its disadvantages,the set up is fastidious and measuring is only possible on the scale from 1 to 10mg/L of dissolved oxygen. The concentration of the original oxygen in the bottle must be 1mg/L which complicates the preparation of the samples. In any case, this measure is not direct and it does not give an immediat the value in mg/L of oxygen.

Photo 1

At about the same time a new procedure for measuring the oxygen appeared in the agro food world. In 2005, this technique, based on chimiluminecsense, attracted the attention of Oenuology Development of Moet & Chandon and of CIVC. At the beginning, the study was focused on experiments to measure the amount of oxygen going through theshipping corks of Champagne. These measurements were made using bottles filled with water (not with because the wine gradually consumes the oxygen as it enters the bottle). The results permit us to follow the evolution of the oxygen's concentration caused by kinetic action of the oxygen after corking. The big advantage of this method is that it is not destructive (it is possible to measure the increase of oxygen over many months in the same bottle) and measures the oxygen concentration (mgl) directly. Repeating measurement of the same bottle over time, permits the measurement of the increase in oxygen and not simply the measure flow assay (dosage LNE). These facts are more significant when these results are not linear.

This article presents the method of measurement used by Moet & Chandon and CIVC, to simulate the measuring of effervescent wines, and obtain the first results. The method will probably be used as a monitoring tool to characterize permeability of different closures to oxygen and to measure the consumption of oxygen in the bottled wines.

Measuring Oxygen By Chimiluminescence

The principal is based on an optical technology. The system is based on a instrument emitting/receiving a light beam directed at one or two sensors. The sensors (also called pastille or dots) are glued to the interior of the bottle before it is filled.

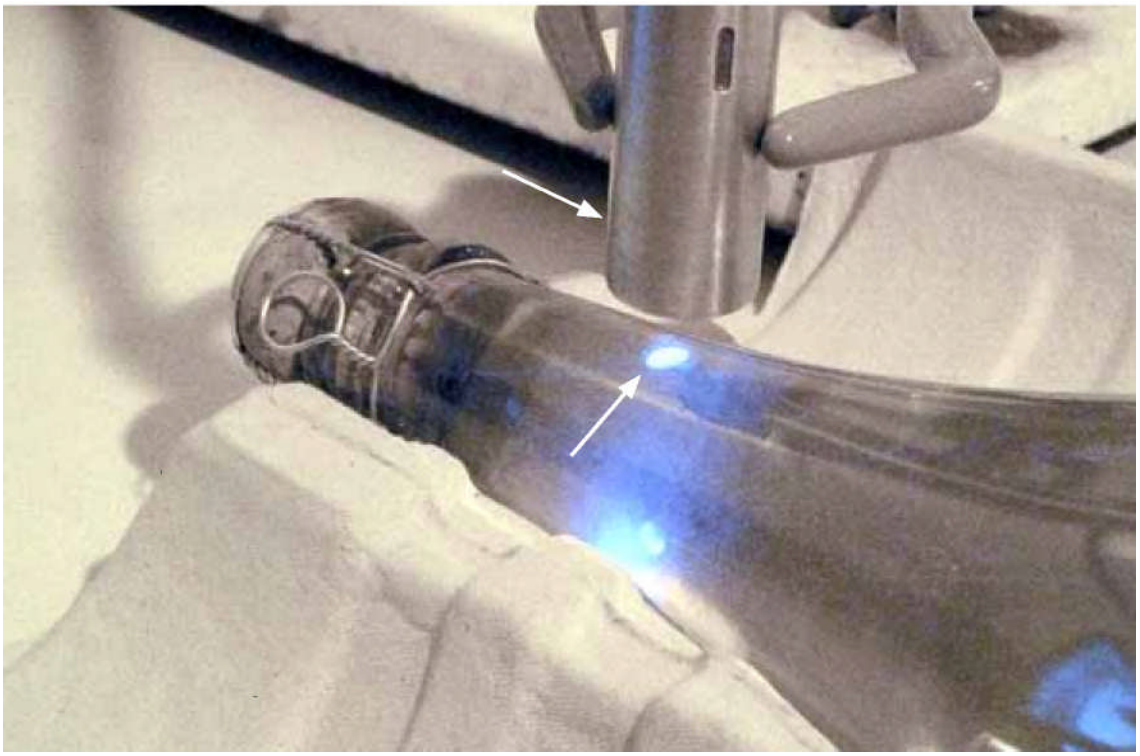

Photo 2

These sensors consist of a fluorescent polymer, which can absorb the luminous energy sent by the light source, and to return it after a certain time in the form of fluorescent light. The measurement is based on the fact that the time to return the fluorescent light is proportionate to the concentration of oxygen present in the proximity of the captor.
In the absence of oxygen, the polymer absorbs the luminous energy sent by the instrument (state of exitation). The measurement is based on the fact that the decay time of the fluorescent light is inversely proportionate to the concentration of oxygen present in the proximity of the captor.

If the oxygen isabsent, the polymer absorbs the luminous energy.

Returning to the fundamentals, figure 1, (the sensors are represented by the red dots, in the presence of oxygen there is a collision between the polymer and the oxygen, with an energy transfer from the sensor to the oxygen . They talk about the phenomenon of quenching of the light by the oxygen. The higher the level of oxygen, the shoter the decay time of the fluorescent signal.

According to the nature of the polmer sensor, the limit of detection of these devices is between 1 ug/l and 15ug/l. The specifications provided by the manufacturers indicate an accuracy of plus or minis 5% of the measured value.

By placing the captor inside the bottle and then filling and corking it, it is possible to measure the change in oxygen concentration over time.

There are a number of different instruments on the market. At CIVC, measurements have been made using the PRESENS-Fibox 3Trace and the OxySense 210T. Our comparative study of the two machines has demonstrated that their performances are comparable. The results presented later in (in this paper) were obtained using the OxySense equipment.

Note: these instruments express the value of dissolved oxygen in ppb, which correspndeds to g/L, or ppm, which is mg/L

Focusing on the Method

PREPARATION OF THE SAMPLE FOR MEASURING

The first step consists of gluing the sensors inside the bottle.

The principal of the method requires working with clear glass bottles to avoid interference of the optical signal due to the color of the glass. The bottles used are clear bottles from Champagne standard of y5cl conforming to the AFNOR standard (NFH 35-056 bottle of Champagne 75cl), whose spec have been verified individually before corking).

DEOXYGINATION

The bottle are filled with 75 cl of demineralize water. The tests can not done in wine because the wine consumes oxygen too rapidly.

For the best results in measuring the ingress of oxygen into the bottles, it is necessary to begin with deoxygenated water. The Development Group at Moet & Chandon was the first to use dry ice to deoxygenate the water. The dry ice has the advantage of deoxygenating both the water, as well as the headspace. Using this method, it is possible to obtain a solution of 50 ppb oxygen with 50 g of dry ice, introduced 5 g at a time. Unfortunately, while effective, this method takes a long time and can be dangerous to the operators.

CIVC has developed an alternative method. It involves the degassing of the water by bubbling it with nitrogen for 15 minutes and flushing the headspace with 5g of dry ice.

Note: it is essential to the cap or cork the bottle as soon as the last piece of dry ice returns to the surface not too soon to avoid the over pressuring of the bottle , or too late to limit the reoxygenating the headspace.

Figure 1
Photo 3

PUT UNDER PRESSURE

To reach the physio-chemical conditions of Champagne, the water bottles are put under internal pressure with a bicarbonate of soda and hydrochloric acid just before corking. The reaction between the two elements releases carbo-dioxide that permits the bottle to attain an internal pressure of 8 bars at 20c.

The corking is accomplished based on the prescriptions and regulations of the CETIE guide #3.

Photo 4

To prevent the a too rapid rise in pressure, bicarbonate is not put directly into the water, but placed in a test tube (photo 4). This technique allows the control of the reaction between the hyrochloric acid and the bicarbonate soda (typically 2-3 days); it equally avoids microbiologic contaminations. Actually, at the start of the reaction, a hydrochloric acid solution of pH1.000, which limits the risk of developing bacteria.

At the end of this reaction, the pH of the water is around 6.00, which are good working conditions for the sensors.

CORKING CONTROLS

The bottle of 29 mm destined to being measured capped eith crowned caps covered with aluminum and synthetics, to be sorted between 31.2 and 31.5mm at the calibre (conforming to the prodceding guide) the diameter is controlled after each corking

CONTROL OF CORKING FOR SHIPPING

After corking the depth of penetration of the cork is measured. The measurements are between 22 and 26 mm, which conforms to the recommendations of the same corking guide.

CONDITIONS OF THE TEST

The first measurements are taken after 24 hours after corking.

It is advised to avoid direct light when taking measurements as it might affect the measurement. The results are based on lots of 5 bottles.

TEMPERATURE CONTROL

The measuring of oxygen using this methodology requires the accurate measurement of temperature. According to Henzy's law: "The higher the temperature rises, the more the soluability of the oxygen diminishes in the water.

An experience of our lab test shows that a change in temperature of 2C generates a change in the measurement of oxygen of 10%. Therefore, if the temperature goes from 16c to 18c, the measurement of oxygen goes from 1000 ppb to 900 ppb (figure 2) It is therefore essential to control the temperature of the solution. To avoid all vaiations due to temperature, the measurement should be be conducted in a temperature controlled space.

(Editor's Note: The OxySense GEN III insruments incorporate an thermocouple for measuring temperature and a software routine that compensates for temperature change, thus there is no longer a need for a temperature constant environment.)

AGITATION

The agitation of the bottle (20 minuted) before the test permits to establishment of an equilibrium liquide and the head space. The amount of oxygen measured as the bottle is lying flat indicates that the oxygen concentration in the liquide phase and not the total oxygen in the bottle.

CHANGES IN OXYGEN READINGS BASED ON TEMPERATURE

The calculations (based on the laws of perfect gas and Henry's Law) show that in equilibrium phase, the oxygen dissolved in the liquid represents only 59% of the quantity of oxygen in the bottle (figure 3). To obtain the total amount of oxygen in the bottle and considering the the amount of oxygen during the fizzy phase, the measurement has to be multiplied by 1.7. For example, if the measurement indicates 100ppb, the total oxygen in the bottle in 170ppb (10).

THE ADDING OF OXYGEN THROUGH THE CORKING DETIRAGE.

Following the process we previously described, we set up a series of clear bottles with sensors, filled them with water, and degassed and pressurized them. They have biduled and topped with three caps of different permeability, chosen according to the measured loses of CO2 established by the LNE.

For each cap studied, the test was conducted on five bottles. The difference in type between the bottles will permits us to evaluate the hetrerogeneity between cap of the same lot for an identical grouping.

The amount of chimiluminescence makes evident the fact that the kinetics of oxygen diffusion through the caps have a rate which could be separated into two phases (figure 4) the first phase during which the ingress of oxygen are very important (expodential phase of 15 to 25 days according to capsule) and a second phase with weaker ingress of oxygen (linear phase)

The laws of diffusion confirm this observation and shows that diffusion of gas through material always occurs during the expondential phase., then a linear one in this order (11).

In the case if capsule, it is possible that one part of the expodntial phase corresponds equally to the part of the bottle after its________ during capsuling.

These results confirm the observations made by LNE to characterize the permeability of the cap of the corking crown that one must wait at least 30 days to be placed in the linear phase.

Over a period of more than 500 days, the measurement show after the expodential phase (not visable on a scale of 500 days) the ingress of oxygen remains linear in that period (figure 5) This observation permits us to extrapolate the intake of oxygen over several years using the measurements achieved over a few months (or days) when the linear phase is reached.

PRESSURE EFFECT

A complementary study was conducted to study the effect of pressure on the ingress of oxygen through different caps. These experiments compare the increase in oxygen between bottles without pressure and those under internal pressure of 8 bars at 20C.

The results, expressed as the ingress of oxygen per 24 hours (Table 1), show that the values differ, notably for the caps most "permeable" where the internal pressure seems to grow significantly with the increase of oxygen.

Note: The indicated value for each ca corresponds to the average increase of oxygen measured over 250 days. Therefore it was decided that the gaseous changes measured by chimiluminescene water with pressure of 8 bars at 20c were more accuat (as described in the method of measuring).

COMPARISON WITH THE VALUES OF LNE

Let us remember that the capsules of triage are actually characterized by their level of gaseous changes expressed by losses of CO_2 in 24 hours. These measures are the results of tests by the National Laboratory of Testing (LNE) at Trappes on the crown corkings executed under standardized conditions in the laboratory (force of compression and diameter settings under control) on bottles with 8 bars of pressure of CO_2 at 20c.

A joint study with LNE shows that the losses of CO_2 and the ingress of oxygen measured by LNE are correlated with a factor varying between 5 to 8 according to the caps, which approaches the coefficients usually obtained in the plastic materials. (pg 46)

Measuring oxygen by chimiluminescence permits the more accurate characterization of caps starting with the real value of the oxygen ingress, rather than an extrapolation from the loss of CO_2.

These results (table 2) are assuring because they permit the classification of the caps as shown in figure 6. This scheme represents respectively the comparison of the measure of losses in CO_2 (measured by LNE in cm^3 CO_2/24 hours) by chimilumenscence.

The obtained values confirm that the corkings most resistant to CO_2 let enter about seven times less oxygen than those more “permeable”.

The cumulative ingress of oxygen varies from 0.2 to 1.8 mg/l/an, values which are very close to those we had indicated in 2007. The kinetics (figure 7) provide us with supplementary information which is the heterogeneity among bottles(symbolized by tracer comprising the average value). This herergeneity among bottle is particularly visible for certain caps, notably for caps 4 and 6, and it seems to grow with time.

After repeating these tests, we will be in a position to furnish data for the total number of capsules on the market, thanks to this method of chimilumenscence.

THE INGRESS OF OXYGEN AND THE CORKING FOR SHIPPING

We will see complications of the problem when dealing with the measurments of the corking entering the bottle. Although the cork is compressed before entering the bottle, it still contains air, and therefore oxygen.

It is also complicated when the material is not homogenous as our traditional cork, consisting of park cork to which glue has been added and two rings of natural cork.

It becomes even more complicated when the material, the cork in this case, is not inert and it frees some “elements’? into the water (as per our test) These elements interfere with the aroma of wine possitively or negatively) and notably as the polyphenols to the reaction of oxidation caused by the presence of oxygen.

We propose to illustrate this case, based on preliminary results (to be confirmed). The Kinetic observed with two corks (traditional) No 1 and 5 from different suppliers, one cork based on microgranulates Cork (cork #6) and the experimental cork entirely synthetic (cork #7)

The Kinetics are presented in photo 8. They permit following comments : whichever type cork enters and leaves in liquid and takes back its shape, an amount of oxygen which represents 2 to 3 mg/l. It is slightly less for a cork based on micro-granuals of cork and also less for a synthetic cork. After this phase the passage of oxygen through a cork made of cork or through a microgranulated cork slows and becomes extremely weak as with a very tight cap. As for the tested synthetic cork the speed with which oxygen enters is very rapid. (2.2 mg/l an) which can have a significant impact on the long period of conservation with this type of cork.

We observe with all the corks of cork, a consumption of oxygen after 200 to 250 days probably due to the reaction of the oxygen with the polyphenol and returned to the water by the cork. The water in these samples is colored.

CONCLUSION

Measuring the changes of oxygen in bottles closed with crown caps or with a shipping cork is currently possible thanks to chimiluminescencee.

The method using deoxygenated water pressurized to 8 bars at a temperature of 20C is very close to the results for the corking of effervesant wines.

The tests have the advantage of being non destructive, and allows the measuring (not the speed of transferring oxygen, but to establish the Kinetics of the oxygen ingress over time, thanks to the variation in concentration of oxygen.

The previously acquired facts lead us to know that the ingress of oxygen varies by a factor of 9 from the most watertights capsules and those most permeable (0.2 to 1.8 mg/ L/an at legal crimping).

The first results for corking for shipping are quite surprising. First of all they show that one traditional cork adds between 2 to 3 mg/L of oxygen to the wine.

This is important because this oxygen is added to the oxygen that penetrates the bottle at time of disgorging. This additional oxygen due to the cork cannot be eliminated by "jetting" (12) and it justifies protection by SO_2 of the liquor.

These early results show that a traditional cork is sufficiently waterproof when the period of desorption has passed. The difference observed between the lot of corks based on cork tied to phase of desorption. Finally, the graphs show the same lot have a relatively homogenous permeability.

These last tests corroborate numerous observations made by professional on cork-corking and for which we have satisfactory explanations. Prudence is recommended as this corking may be variable according to the conditions of fabrication, its physical characteristics and also its change over time due to contact with wine.

The results of current studies should permit us to learn more about these different phenomenon.

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Bibliographie

(1) Suivi de l'oxygène des phases gazeuse et liquide de bouteilles de vin à l'embouteillage et en conservation.
Vidal J-Cl., Moutounet M. (2006). Journal International Scientifique Vigne et Vin, 40, n°1, 35-35.

(2) Capsules de tirage et vieillissement des champagnes.
Tribaut-Sohier I., Valade M.
Le Vigneron Champenois, 1999, n° 2, p. 47-62.

(3) Capsules de tirage à joint synthétique : des fournitures très importantes. Tribaut-Sohier I., Valade M.
Le Vigneron Champenois, 2001, n° 11, p. 50-77.

(4) Les apports d'oxygène en vinification et leur impact sur les vins – 1ère partie. Valade M., Tribaut-Sohier I., Bunner D., Pierlot Cl., Moncomble D., Tusseau D. et le laboratoire d'analyse des Services Techniques du CIVC.
Revue française d'œnologie, n° 221.

(5) Les apports d'oxygène en vinification et leur impact sur les vins – 2e partie.
Valade M., Tribaut-Sohier I., Bunner D., Laurent M., Moncomble D., Tusseau D. et le laboratoire d'analyse des Services Techniques du CIVC.
Revue française d'œnologie, n° 222.

(6) Les capsules de tirage à joint synthétique. Les capsules sur le marché en 2009. Langleron E., Valade M., Moncomble D. Le Vigneron Champenois, 2008, n° 11, p. 54-57.

(7) Non destructive colorimétric method to determine the oxygen diffusion rate through closures used in winemaking. Lopes P., Saucier C., Glories Y. (2005). Journal of Food Chemistry, 53, 6967- 6973.

(8) Impact of storage position on oxygen ingress trough different closures into wines bottles.
Lopes P., Saucier C., Teissedre P.-L., Glories Y.
(2006).

(9) Bouchage de tirage et d'expédition pour vins mousseux de qualité produits dans des régions déterminées VMQPRD sur bague couronne NF H35-029,
Document INE 93/006, édition 1994. Guide n° 3 du CETIE.

(10) Oxygène et homogénéisation des vins au dégorgement.
Bunner D., Tribaut-Sohier I., Valade M., Rouchaussé J.-M., Tusseau D., Moncomble D.
Le Vigneron Champenois, 2008, n° 4, p. 40-63.

(11) Les gaz dans la bouteille.
Robillard B., Liger-Belair G.
Revue des Œnologues, 2008, n° 126.

(12) Inertage au dégorgement.
Bunner D., Tribaut-Sohier I., Valade M., Rouchaussé J.-M., Tusseau D., Moncomble D.
Le Vigneron Champenois, 2008, n° 6, p. 36-54.