Search for an analytical method adapted to OTR measurement of stoppers after long-term bottle ageing

Alexandre Pons[1,2], Christophe Loisel[3]
[1] *Tonnellerie Seguin Moreau – Cognac – France.* [2] *Unité de recherche œnologie – EA 4577 – USC 1366 INRAE ISVV- Univ. de Bordeaux – Villenave-d'Ornon – France.* [3] *Diam Bouchage – Céret – France.*

Extract from the Revue des Œnologues n° 180
search.oeno.tm.fr

Introduction

Our recent work has made it possible to determine the impact of the stopper's OTR (Oxygen Transmission Rate) on the evolution of the aroma of white Sauvignon Blanc wines during long-term ageing for 10 years *(Pons et al., 2019)* and of rosé wines for a period of three years *(Cayla et al., 2019)*. Today, this physical characteristic of stoppers is quite often evaluated by means of the luminescence method, known as the Presens method *(Diéval et al., 2011)*. This method is applied most often to the OTR measurement of stoppers early in ageing for a transmission level between less than 0.1 mg/year up to more than 40 mg/year *(Robertson, 2009)*. Tin-lined screw caps are known to provide the tightest seal, whereas natural cork stoppers can show extreme variations in OTR level, owing to their structural heterogeneity.

As such, in order to expand our knowledge of OTR stability during ageing, as well as its impact on wine colour, aroma and flavour, we present here the results of a comparative study of protocols applied to OTR measurements on a number of "aged" stoppers from a variety of studies.

Materials and methods

Presentation of the stopper OTR measurement technique by coulometry

The comparative study of OTR measurement protocols using coulometry (COUL) was done by two independent laboratories using an absolute coulometric sensor. This technique is currently used in the industry for the OTR measurement of packaging (ASTM D 3985 and ISO 15105-2 standards: 2003). More recently, it was applied to OTR measurement on stoppers in accordance with the following protocol. After being cut, the neck of the bottle is sealed on a rigid metal support, making it possible to introduce a flow of nitrogen (carrier gas) around the bottleneck, thus in contact of the stopper surface. The outer part of the stopper is either left in the open air (O_2, 21%) or connected to a pure oxygen source (O_2, 100%). The quantity of oxygen migrating through the test stopper is entrained by the carrier gas towards the detector.

Upstream from the OTR measurement itself, it is essential to include a degassing period of one to three months. This enables elimination of residual oxygen present in the lenticels of natural cork stoppers, which would otherwise lead to an overestimate in the measurement. During this step, the carrier gas – nitrogen in our experiments – can be used dry (S) or humid (H). Once this degassing step has been completed, the OTR measurement can begin. The characteristics of the coulometric measurement methods (COUL) selected for this project are as follows. The COUL 1 method uses air and dry nitrogen during the desorption phase. The COUL 2 uses pure oxygen and humid nitrogen. The COUL 3 method corresponds to a hybrid between the COUL 1 and COUL 2 methods, using humid nitrogen and air.

Table 1: Characteristics and distribution of selected stoppers (x) **for ageing of Sauvignon Blanc wines** (Study 1, 11 years) **and rosé wines** (Study 2, three years).

Stoppers	OTR (mg O_2/year)	Wines	
		Sauvignon Blanc	Rosé
Saran cap	< 0.1[2]	x	-
Diam 30-P0.07	0.3[2]	x	x
Diam D5-P0.15	0.4[2]	x	x
Saranex cap	0.5[2]	x	-
Diam D5-P0.35	0.6[2]	x	-
Synthetic 1	0.6[2]	x	-
Synthetic 2	1.1[2]	-	x
Synthetic 3	1.5[2]	x	
Synthetic 4	4.6[2]	x	-
Natural cork	0.1 – 40[1]	x	x

[1] *Roberston (2009).*
[2] *OTR values found on the suppliers' technical data sheets.*

Choice of wines

Study 1 – Determination of stopper OTR after 11 years of bottle ageing

The wine samples selected for this study come from an experiment conducted on different Sauvignon Blanc wines closed with natural cork stoppers and eight other stoppers: three Diam micro-agglomerated cork stoppers with increasing OTR values (Diam 30 P0.07, Diam 5 P0.15, Diam 5 P0.35), three synthetic stoppers and two screw caps *(Pons et al., 2019)*. The OTR values of each of the stoppers are presented in ***Table 1.***

Study 2 – OTR determination of selected stoppers for bottle ageing of rosé wines for three years

These wine samples come from a previously described project *(Cayla et al., 2019)*. The goal was to compare the evolution of rosé wines aged with two micro-agglomerated corks (Diam 30 P0.07, Diam 5 P0.35), a synthetic stopper and a natural cork stopper. All of the synthetic stoppers from these two studies are numbered from 1 to 4 based on increasing OTR level.

Results

Evaluation of OTR for nine different stoppers after 11 years of bottle ageing (COUL1 method)

Initially, all of the wine samples from Study 1 were analysed with the COUL 1 method, i.e. by using dry N_2 and 21% O_2 (ambient air). As presented in ***Figure 1,*** we show that the OTR range encountered after 11 years of bottle ageing is extremely large, from 0.07 mg/year for the Saran tin-lined cap to more than 120 mg/year for one of the natural cork stoppers. The median values can be structured in three groups. The first group which has an OTR level less than 1 mg/year includes the screw caps, the Diam 30-P0.07 micro-agglomerated cork stopper and the Synthetic 1 stopper. The second group, between 3 and 6 mg/year, includes the Synthetic 3 stopper and the D5-P0.15 micro-agglomerated cork stopper. The third and last group has higher OTR levels, from 6 to 7 mg/year, and includes the D5-P0.35 and Synthetic 4 stoppers as well as the natural cork stoppers.

Screw caps are known for their low OTR, and we confirm this result for the Saran capsule after 11 years of bottle ageing ***(Figure 1A).*** However, for the Saranex screw cap, the measured OTR range is quite wide. Since these stoppers are produced on an industrial scale, this result is quite surprising. It quite likely illustrates an impact on the cap that occurred during bottle ageing. After 11 years of bottle ageing, the synthetic stoppers have OTR levels that are substantially higher that at the start of the trial. However, the ranking of stoppers as a function of their OTRT0 remains unchanged. As such, the COUL 1 method is suitable for the OTR measurement of synthetic stoppers and screw caps after a long period of bottle ageing.

For the performance of cork stoppers, we show that the ranking of micro-agglomerated cork stoppers is similar to that described at the start of the project ***(Table 1),*** i.e. OTRD30-P0.07 > OTRD5-P0.15 > OTRD5-P0.35. After 11 years of bottle ageing, the distribution of OTR values for the D30-P0.07 stopper remains much lower than 0.8 mg/year, very close to the initial technical characteristics (0.3 mg/year). This stopper type offers the guarantee of a known, low level of oxygen addition throughout the wine's lifetime: from bottling until it is opened for tasting.

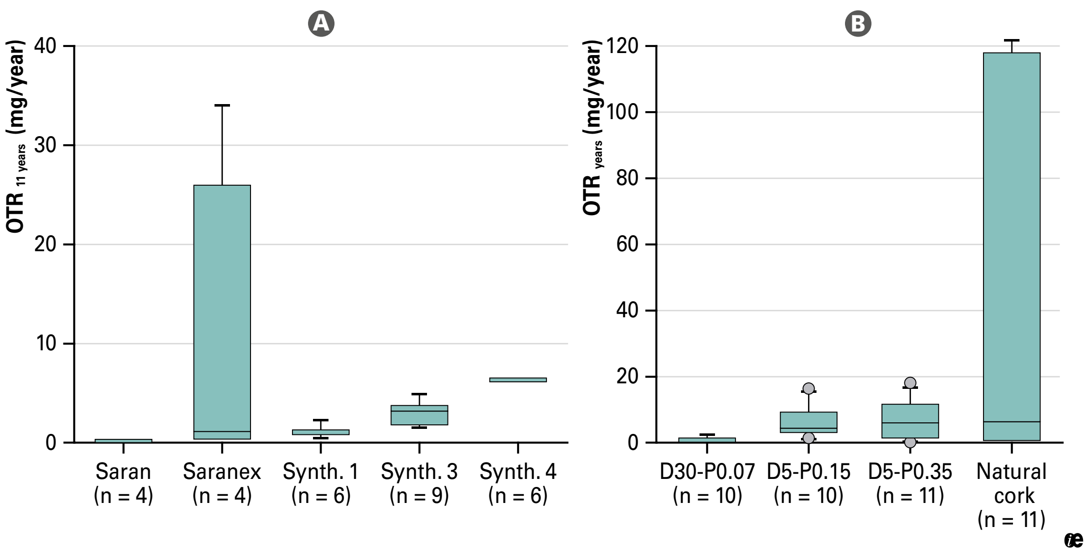
However, for the other three stoppers, the measured values are rather high or even quite high for natural cork stoppers ***(Figure 1B).*** Such results may have their source in the application of the measurement method. In fact, the laboratory that applies the COUL 1 method uses dry nitrogen for the desorption of oxygen present in the stopper. As mentioned previously, this phase can last several months. As such, it cannot be excluded that the cork stoppers with a variable moisture (impregnation) level may dry out during this phase, thus provoking, as an artefact, a significant overestimate of the real OTR value of natural cork and micro-agglomerated cork stoppers. This type of phenomenon quite likely explains what we observed after 11 years of bottle ageing for a number of cork stoppers. As such, we propose comparing the results from the COUL 1 method for a selection of four stoppers with different OTR values with those from another laboratory using humid nitrogen for desorption and pure oxygen during the measurement (COUL 2 method).

Impact of moisture in the nitrogen used during the desorption phase on the OTR measurement

The results of the impact of the measurement method on the stopper's OTR value are presented in Table 2. We show that the OTR results obtained at 11 years with the COUL 1 and COUL 2 methods are higher on average than the OTRT0 values. Furthermore, depending on the method used, the ranking of stoppers as a function of their OTRT0 value is not systematically followed. Some values are, in fact, surprising. For example, this is the case for the sample with an OTR value of 18.2 mg/year with the COUL 1 method and 0.9 mg/year with the COUL 2 method (the results are corrected to 21% O_2). It cannot be excluded that this type of stopper takes on moisture during bottle ageing and that the application of the sample preparation protocol has dried it out. As such, these results confirm the importance of using humid nitrogen to prevent the cork stoppers from drying out during the measurement.

In ***Table 2,*** we deliberately corrected the OTR results obtained with pure oxygen (100%) to 21% oxygen in order to make compa-

■ Figure 1: Distribution of OTR values at 11 years for Ⓐ synthetic stoppers and screw caps, Ⓑ natural cork and micro-agglomerate cork stoppers, obtained by the COUL 1 method (dry N_2, 21% O_2). The horizontal line corresponds to the median value of each group.

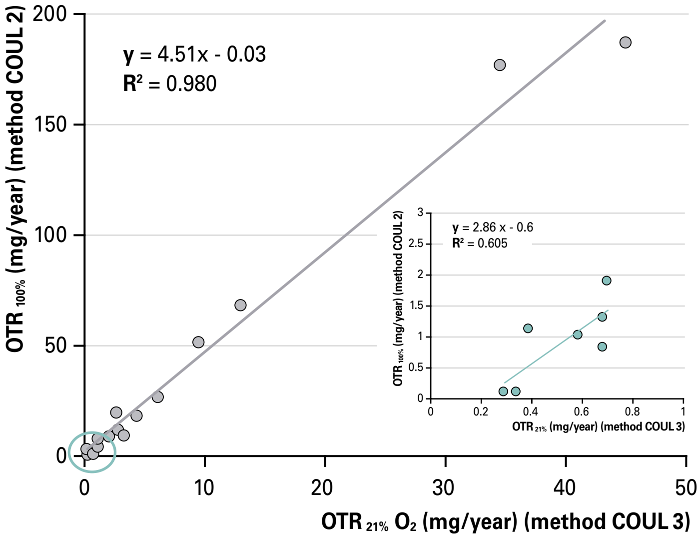


■ Table 2: Comparison of mean OTR levels (mg/year) **of micro-agglomerated cork and synthetic stoppers after 11 years of bottle ageing as a function of method type.**

Date	Method	Exterior [O_2]	OTR (mg/year)			
			D30-P0.07	D5-P0.15	D5-P0.35	Synth. 4
T0 [1,2]	/	/	0.3	0.4	0.6	4.6
11 years	COUL 1 (dry N_2)	21 %	1.6	18.2	3.2	5.7
	COUL 2 (humid N_2)	100 % (21 %) [2]	0.5 (0.1) [2]	4.2 (0.9)	8.2 (1.7)	48.9 (10.3)

[1] *OTR values found on technical data sheets in 2008.* [2] *Calculated OTR values corresponding to an exterior [O_2] of 21%.*

■ **Figure 2: Correlation between the OTR values obtained by the COUL 2 technique** (humid N_2, 100% O_2) **and COUL 3** (humid N_2, 21% O_2) **for natural cork and micro-agglomerated cork stoppers** (at 11 years) (n = 20).



rison of the two methods easier. From a theoretical standpoint, it is possible to approximate an OTR measurement in ambient air by dividing all values obtained at 100% by 4.76. However, is this hypothesis valid throughout the entire OTR range of stoppers used for wine ageing in bottles? Can we really apply this factor with the simple goal of better evaluating the real quantity of oxygen that the wine will receive? To answer this question, we asked the laboratory to analyse the same bottles of wine corked with natural cork and micro-agglomerated cork stoppers, successively with ambient air and pure oxygen in controlled moisture conditions.

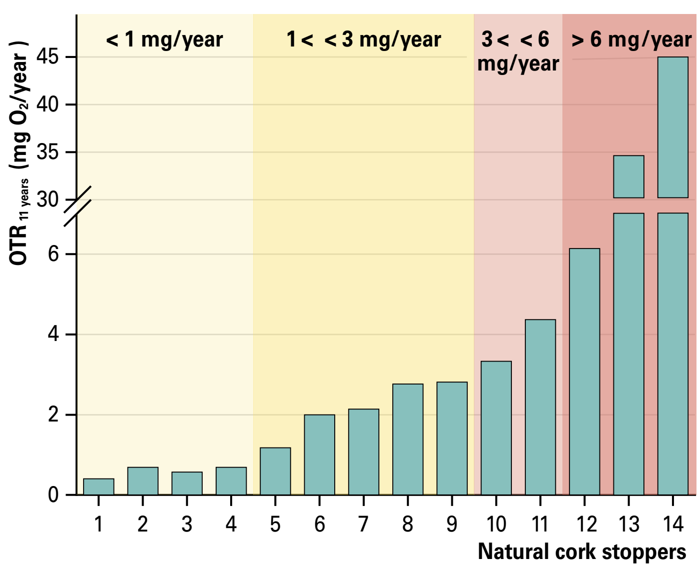
As we show in ***Figure 2,*** the hypothesis is valid for high OTR values (OTR100 % > 2 mg/year) but remains less robust for low values. There are two reasons for this. First of all, the low OTR values approach the detection limits of the apparatus and consequently, the error associated with the measurement is greater. Then, another parameter to take into account is the necessary desorption time to reach equilibrium: it is often greater for the measurement at 100% O_2. In this event, it cannot be excluded that the measurement may be affected, whereas the equilibrium phase is not completely reached. All of these elements point to the importance of knowing the operating conditions of the OTR measurement in order to interpret the results in oenological terms. For this reason, we recommend an OTR measurement with humid nitrogen and ambient air for old cork stoppers (COUL 3), in order to simulate the conditions of wine ageing in bottles.

Application of the optimised coulometric measurement method for determination of OTR with various cork and synthetic stoppers after 11 years and three years of bottle ageing

In this last part, we present the results of the two previously described studies for which the OTR values of stoppers were determined with the COUL 3 method. One corresponds to bottle ageing of Sauvignon Blanc wines for 11 years, the other to bottle ageing of rosé wines for three years.

For the first study, we analysed 14 natural cork stoppers selected for the bottle ageing of the same Sauvignon Blanc wine. The OTR results presented in ***Figure 3*** illustrate the great heterogeneity of natural cork after 11 years of bottle ageing. However, the range of values is less extensive than with the COUL 2 method ***(Figure 1).*** This illustrates the interest of desorption using humid nitrogen. The measured OTR range is between 0.38 and 44.9 mg/year, whereas the median value of this distribution is 2.5 mg/year. As such, 28.5% of the stoppers have an OTR value < 1 mg/year, 36% have an OTR value between

■ **Figure 3: OTR values** (COUL 3 method, humid N_2, 21% O_2) **of natural cork stoppers selected for the ageing of a Sauvignon Blanc wine after 11 years of bottle ageing** (n = 14). Representation of OTR levels in increasing order and structured in four classes.



1 and 3 mg/year, 14% have an OTR value between 3 and 6 mg/year and 21.5% have an OTR value greater than 6 mg/year, which most likely leads to premature oxidation of these white wines.

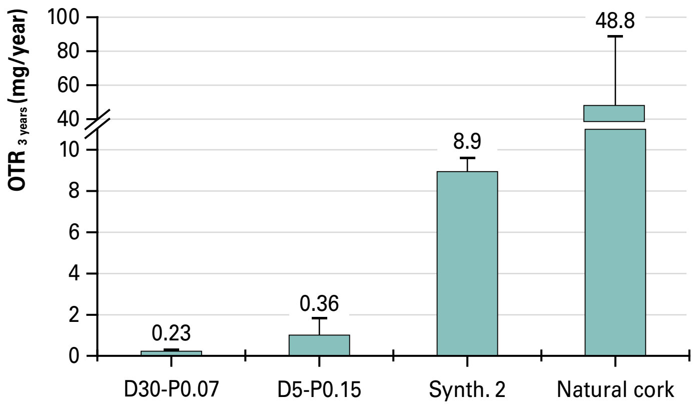
For the second study, we selected four stoppers for the bottle ageing of rosé wines. After three years of bottle ageing, micro-agglomerated cork stoppers display performance levels similar to those for a new stopper ***(Figure 4).*** In contrast, the synthetic stopper (Synth. 2) has an OTR value nearly nine times greater than the one it had at the start of the project. At this stage of bottle ageing, the natural cork stopper and the synthetic stopper have an OTR value much greater than the others, which could indicate faster oxidative ageing of rosé wines with these stopper types.

Conclusion

The goal of this study was to identify a suitable measurement protocol for determining OTR in bottles aged for a number of years. After having tested a variety of approaches, we show that the coulometric method is perfectly adapted to this goal, while also revealing the impact of stopper preparation on measurement quality. The hydration control of the stopper during the desorption phase has been shown to be a crucial parameter for cork stoppers, as it affects the precision of results. We have shown in precise terms that based on our selection of cork stoppers, the OTR levels after 11 years of bottle ageing are between 0.07 mg/year and 44.9 mg/year. In light of these OTR values, it is quite likely that the composition of the wine is profoundly affected by this oxygen transmission.

Editor's note: *The bibliography for this article is available on the Revue des Œnologues website:* ***search.oeno.tm.fr***

Figure 4: Comparison of theoretical mean OTR values (OTR T0) **of micro-agglomerated cork, synthetic and natural cork stoppers, to those measured after three years of bottle ageing** (COUL 3 method, humid N_2, 21% O_2). The values corresponding to the mean of each stopper group (n = 3).



	D30-P0.07	D5-P0.15	Synth. 2	Natural cork
OTRT0 (mg/year)	0.3	0.4	1.1	/

Article published with the authorization of the Journal the Revue des Œnologue
N° 180 - July 2021– pages 50 to 53
"Search for an analytical method adapted to OTR measurement of stoppers after long-term bottle ageing" Alexandre Pons, Christophe Loisel.
The international reference for scientific and technical news on grape growing and winemarking, for more than 40 years in, France and 60 countries.
■ More than 6,000 articles archived by keywords search.oeno.tm.fr
■ Contact us : infos@mail.oeno.tm.fr ■

revue des
œnologues
Science and techniques of grapevine and wine
et des techniques vitivinicoles et œnologiques

search.oeno.tm.fr

Viticulture | Winemaking | Œnology | Conditioning | Sensory analysis

The quarterly journal of the wine professionals sector

Scientific & technical news

- **For more than 40 years,** in 60 countries
- **An international journal** in french
- **Viticulture** | Œnology | **Conditioning**

The quarterly journal of the wine professionals sector

"Our readers are looking for **reliable information** and **specific technical advice** to achieve **concrete investments** and implement **operational solutions** in viticulture and œnology.

Now more than ever, it is essential to be **well informed** and by true professionals aware **of technical issues** of our sector".

Henri-Laurent Arnould
Agronomist-Œnologue
Director of the Revue des Œnologues

At the source of the information

- **Free access to a large corpus of scientific & technical information**
- Information **evaluated** and **selected** for more than 40 years by the **Revue des Œnologues**

Faster to the point…

- **Quick access** by **keywords**
- Abstracts, bibliographies, lists of articles
- More than **6,000 articles** and **5,000 contributors**

search.oeno.tm.fr
Search engine | Viticulture
Œnology | **Revue des Œnologues**