Characterization of the oxygen transfer rate of "new-ancient" natural materials in wine maturation containers

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Abstract

Today there is a trend in oenology that promotes the use back to old natural materials for the manufacture of storage and maturation wine tanks. One of the most sought-after characteristics of these materials is their permeability to oxygen from air to improve wines without becoming a harmful process. The reference performance without discussion is the oak barrel for its ability to oxidize wines in a controlled way improving them. In this way, it would be possible to carry out this process of maturing wines in containers in which the use of wood is not obligatory, as is the case with oak barrels or foudres. In this work, the results of the oxygen permeation analysis are presented, under test conditions typical of a tank, of materials such as stoneware, ceramics (qvevri), concrete and granite.

The natural materials can be divided into two classes, which are formulated based on different components such as ceramics (qvevri), gress and concrete (considered a natural material), and on the other hand is the stone, although a composite material, its composition is not modifiable and depends on its origin. The oxygen permeability of the materials tested has been very diverse, typical of natural materials. The results show that the ceramic (qvevri) presents an excessive permeability, not only to atmospheric oxygen, but also to liquids and needs a treatment to be able to be used in liquid containers. Gress and concrete, can be impermeable to the liquids but they maintain a permeability to the atmospheric oxygen that makes them candidates for its use in permeable tanks for wine aging. Finally, granite has some very interesting characteristics and it is necessary to use thickness control looking for the desired oxygen transmission rate.

Introduction

The knowledge of the oxygen permeability of the air of storage tanks and wine maturation is of great interest in oenology.

Most of the published data on oxygen permeation of these materials do not correspond to the situation in a container filled with wine, where the driving force for oxygen inlet is the difference in concentrations on both sides of the wall (Figure 1).

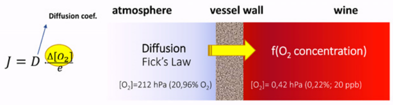


Figure 1: barrel, tank or vessel scenario

Materials & Methods

In this work we have analyzed four materials that we will denominate "natural" that are present in the offer of containers for the storage/ageing of wines with or without the addition of wood.

Two different procedures have been used to test the materials, both based on ASTM F3136 - 15: Standard Test Method for Oxygen Gas Transmission Rate through Plastic Film and Sheeting using a Dynamic Accumulation Method. To this end, work has been carried out with a system that allows the measurement of porous materials with a high thickness.

OTR measurement

The oxygen permeation is performed measuring the increase in the oxygen partial pressure with time (hPa/day), which allows the determination of the OTR using the law of ideal gases.

$$OTR = \frac{\Delta n \cdot V_m}{\Delta t} = \frac{\Delta p_{O2} \cdot V}{R \cdot T} \cdot \frac{V_m}{\Delta t} = \frac{\Delta p_{O2} \cdot V}{\Delta t \cdot P_{atm}}$$

where n is the amount of a substance in moles, V_m is the molar volume of oxygen, T is the absolute temperature in ºK, $\frac{\Delta p_{O2}}{\Delta t}$ is the slope in the linear part of hPa/day, V is the device's chamber volume, and P_{atm} is the atmospheric pressure in hPa during the assay.

Oxygen partial pressure measurement

The measurement of dissolved oxygen in the device was performed using an Oxytrace device (PreSens GmbH, Germany) equipped with a PSt6 oxygen sensor (measurement range 0 – 41.4 hPa, detection limit 0.002% O_2). This sensor was placed inside the device in direct contact with the fluid of the chamber that, according to the test, was nitrogen or synthetic wine. Luminescent measurements were performed using an optical fiber through a transparent surface where the sensor was attached.

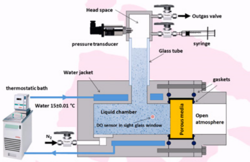
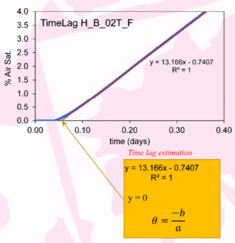


Figure 2: Measurement device scheme

Calibration of the oxygen systems was performed using a conventional two-point calibration in the model wine saturated with nitrogen (cal 0) and a second value in the range between 5 and 10% air saturation. A calibration gas mixture with 2.001% (±0.5% rel) pure oxygen gas and nitrogen (9.55% air-sat) was used as a second calibration standard. (del Alamo, M., & Nevares, I. 2012).

Figure 3: Setup of eight measurement devices



Diffusion coefficient: $D\left(cm^2/s\right) = \frac{e^2}{6.\theta}$

Permeability coefficient: $P\left(\frac{cm^3(STP).cm}{cm^2.s.Pa}\right) = D\left(cm^2/s\right).S\left(\frac{cm^3(STP)}{cm^3.Pa}\right)$

Sorption coefficient $S\left(\frac{cm^3(STP)}{cm^3.Pa}\right) = \frac{P\left(\frac{cm^3(STP).cm}{cm^2.s.Pa}\right)}{D\left(cm^2/s\right)}$

Ceramic Qvevri

Three samples of qvevri ceramics from different wine regions of Georgia have been analyzed. Several pieces of each of the ceramics were extracted and were tested in different conditions: dry and wet. After that all of them were dried and the waxing procedure were also tested. Pure bee wax were used, and applied to the "wine" side of each piece. To apply the wax, the ceramics were heated at 120ºC and the molten wax was applied to the surface for several hours in a stove. This operation was repeated several times until the ceramic did not admit any more wax. Between each of the applications the pieces were analyzed to measure the flow of oxygen permeating them.

Figure 4: Ceramic Qvevri samples

Figure 5: waxed ceramic Qvevri samples

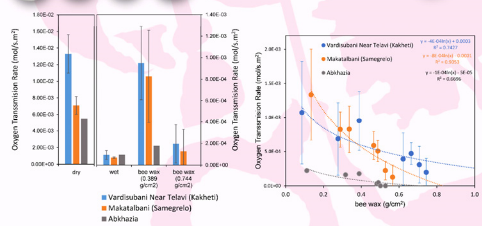


Figure 6: Ceramic Qvevri OTR measurement

Stoneware

Is a sintered, homogeneous and compact ceramic that is inherently nonporous and similar to natural granite in many aspects. It can be fired once or twice to produce a better quality fired glaze finish. Maximum firing temperatures can vary significantly and, typically, temperatures will be between 1180 and 1280°C. Earthenware may be tailored with controlled heating treatments to offer unique gas and moisture permeation properties. Stoneware is practically impermeable to liquids (water absorption ≤1%) (Martín-Márquez, et al 2008). Impermeability prevents wine evaporation, which would allow periodic topping, although it permits micro-oxygenation of the liquid inside.

Stoneware tank and different stoneware pieces have been measured.

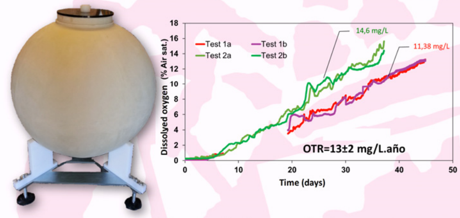


Figure 7: Stoneware tank and oxygen transfer rate measurement

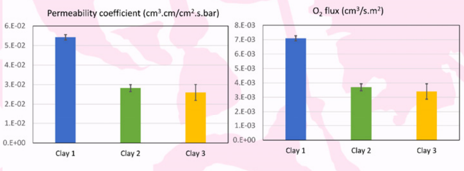


Figure 8: Permeability coefficient and O_2 flux of different stoneware pieces

Concrete

Another product widely used in winemaking is concrete, similar to stoneware from the point of view of its waterproofing and thermal insulation, but less stable because it solidifies at room temperature. Concrete is permeable to oxygen, which makes it a material of interest for containers that micro-oxygenate wines, thus preventing any leaks. The permeability of plain concrete to oxygen is $k = 5 \div 11 \times 10^{-11}$ m/s, between the different binders and water/binder ratios (Salvoldi et al., 2015). The permeability of concrete is mainly affected by its pore structure system. But all the data founded in bibliography use the pressure method to measure concrete permeability, a method that does not reproduce the usual conditions produced in wine containers. This test system uses a pressure difference and works with pure oxygen.

In order to know the oxygen permeability of the concrete used in wine tanks, concrete samples were obtained from wine tanks that were tested using the time-lag method, in which the driving force of oxygen permeation was the difference in concentration.

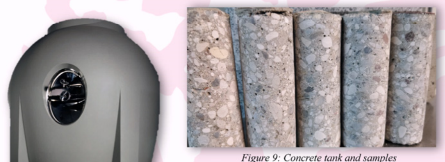
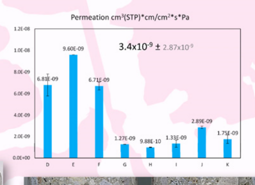


Figure 9: Concrete tank and samples



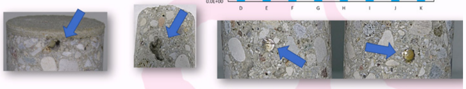


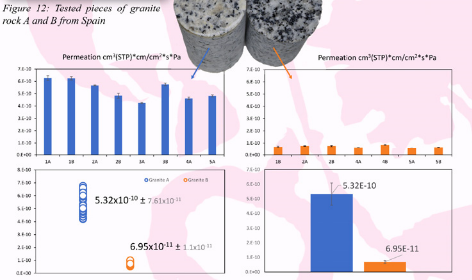
Figure 10: detail of different concrete "defects" that can have an effect on oxygen diffusion

Granite

Is a sintered, homogeneous and compact ceramic that is inherently nonporous and similar to natural granite in many aspects.

Figure 12: Tested pieces of granite rock A and B from Spain

Figure 11: "Stone barrel" made with granite rock



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