# Wine absorption by cork stoppers

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## Abstract

To evaluate the magnitude of wine absorption by cork under conditions as close to reality as possible and its evolution in time, ready-to-use natural cork stoppers and "1+1" cork stoppers were used to close bottles filled with red wine. Stoppers were removed after 3, 6, 12 and 24 months of contact to determine absorption of liquid and liquid progression along the lateral surface of the cork stopper. Variation of absorption with contact time was studied by adjusting the model Absorption = $a\sqrt{t}$ ($R^2$: 82.19 - 93.63%). A scheme of the evolution of wine absorption with time is proposed, differentiating liquid flow along cork-glass interface, diffusion in cell walls and liquid flow through the cell lumens. In conditions of use, a value of $4.48 \cdot 10^{-13}$ m$^2$ s$^{-1}$ was obtained for non-radial diffusion coefficient (D).

**Additional key words**: cork-wine interaction, diffusion, natural cork stopper, technical cork stopper.

## Resumen

### Absorción de vino por los tapones de corcho

El objetivo del presente trabajo fue evaluar la magnitud de la absorción de vino por el corcho en condiciones reales y su evolución con el tiempo. Para ello, se utilizaron tapones de corcho acabados, naturales y "1+1" para cerrar botellas de vino tinto. Los tapones fueron extraídos después de 3, 6, 12 y 24 meses de contacto con el vino y se determinó la absorción y la progresión del líquido por la superficie lateral del tapón. Para estudiar la variación de la absorción con el tiempo, se ajustaron modelos del tipo Absorción = $a\sqrt{t}$ ($R^2$: 82,19 - 93,63%). Se presenta un esquema de esta evolución, diferenciando el flujo de líquido a lo largo de la superficie corcho-vidrio, la difusión en las paredes celulares y el flujo de líquido a través del lumen de las células de corcho, obteniéndose un valor de $4,48 \cdot 10^{-13}$ m$^2$ s$^{-1}$ para el coeficiente de difusión en dirección no radial para el corcho en condiciones de uso.

**Palabras clave adicionales**: difusión, interacción corcho-vino, tapón de corcho natural, tapón de corcho técnico.

*To Prof. M. M. A. Fortes, in memoriam*

## Introduction

Cork is used in enology due to the unique physical-mechanical and chemical properties of the material including impermeability and mechanical behavior. These properties guarantee the maintenance of liquid tightness for prolonged periods of time, as well as a minimal cork-wine interaction (Maga and Puech, 2005; Silva *et al.,* 2005). Despite its low intensity, the influence of this interaction on the evolution of bottled wine is outstanding, as shown by the numerous studies published on the transfer and absorption of volatile compounds by cork stoppers and the effect of the stopper system on wine micro-oxygenation (Juanola *et al.,* 2005; Lopes *et al.,* 2005; Skouroumounis *et al.,* 2005).

This work is focused on a less studied aspect: absorption of liquids by the cork stopper. The interest in the absorption phenomenon is due to the fact that it notably

Abbreviations used: CETIE (Centre Technique International de l'Embouteillage et du Conditionnement), RH (relative humidity), SE (standard error).

alters the behavior and properties of cork, a hygroscopic material. From a mechanical point of view, absorption has opposing effects: on the one hand, it increases the volume of the cork stopper, thus raising pressure on the neck of the bottle; on the other hand, increased moisture content diminishes compression stress against the glass, an effect which adds to that of the relaxation phenomena characteristic of viscoelastic materials (Fortes *et al.,* 2004). From a physical-chemical point of view, in cork as in wood (Siau, 1984), increased moisture content is expected to increase the diffusion coefficient, thus facilitating molecular exchange between the matrix (cork) and the solvent (wine).

Scarce literature has been found on this subject, which is why it was important to characterize the evolution in time of the cork-wine interaction by measuring the amount of liquid retained by the cork (absorption). The absorption study was based on Siau's (1984) model for wood, which assumes that transport of liquids through tissue is the result of two physical phenomena:

a) Diffusion of fluid through the material, including both gaseous diffusion (vapor transfer through cellular lumina) and diffusion through the cell wall. This phenomenon is the consequence of a gradient of concentration (moisture) between the two ends of the cork stopper. Diffusion stops when all cell walls are saturated, and gradient disappears. According to Fortes *et al.* (2004, p. 187), cell saturation is complete when absorption gets to 60%. Like other similar processes, this is regulated by Fick's law, which represents the relation between flow and the gradient of concentration (moisture in this case) in steady-state conditions by means of the diffusion coefficient *D*. The value of this coefficient for water absorption by cork at room temperature is extremely low (about $10^{-11}$-$10^{-12}$ $m^2$ $s^{-1}$) (Rosa and Fortes, 1993) and is affected by many factors, such as the relative position of the cork tissue with respect to the direction of progression of liquid, temperature (Skurray *et al.,* 2000a), and moisture content (Siau, 1984). The relative position of the tissue varies with the type of cork stopper used: in the traditional cork stopper (commercially identified as "one-piece natural"), the radial direction of the tissue is perpendicular to the direction of advance of the liquid, whereas in disc-ended cork stoppers ("1+1" type) both directions are parallel. Recent studies on samples with very low moisture content (3.5%) yielded *D* coefficient values one or two orders of magnitude lower ($10^{-13}$ $m^2$ $s^{-1}$) than those cited (Marat-Mendes and Neagu, 2003; Marat-Mendes and Eugen, 2004).

b) Flow of liquid through the tissue interstices, under the influence of a pressure gradient, which can be static or capillary. This is a permeability phenomenon, to which cork is highly resistant due to its chemical composition and cellular structure. The most important channels are the pores, which are oriented differently in natural cork stoppers and "1+1" cork stoppers, and have much larger dimensions than those required for capillarity phenomena. In addition, one must consider the presence of small intercellular communication conduits of less than 1 μm, in which capillarity phenomena can take place (Pereira, 2007).

This study was undertaken to evaluate the magnitude of absorption phenomena under conditions as close to reality as possible, to study their evolution in time, and to describe accordingly the transport of liquid through the cork stopper.

## Material and methods

Two types of cork stoppers were used: natural (first quality) and "1+1" (agglomerated body with one disc glued on both ends). All samples were provided by Catalonian Cork Institute (ICSuro, Palafrugell, Girona, Spain). Nominal dimensions were 24 mm (diameter) and 44 mm (length) for both types. As discussed above, the main direction of progression of liquid is perpendicular to the pores in natural cork stoppers, whereas it is parallel to the pores in natural cork discs of "1+1" stoppers. All cork stoppers were rinsed in water in a rotating drum, washed with hydrogen peroxide and finished by spraying with an aqueous emulsion of paraffin and silicone (a mixture of polydimethylsiloxane, inert fillers, food-grade pigments, paraffin, and teflon).

Burgundy bottles (750-mL capacity) were filled with a young red wine (Catalonia designation of origin). The bottling process was carried out in a winery under routine industrial conditions.

All bottles had a CETIE (Centre Technique International de l'Embouteillage et du Conditionnement) neck with standardized inner dimensions. Cork stoppers were conditioned to 20°C and 65% relative humidity (RH) and weighted before bottling. After bottling, bottles were left standing for 24 h and then were laid down and stored in horizontal position at 16°C ± 2°C and 55% RH ± 15% RH until the cork stopper was removed. Measurements were made after 3, 6, 12, and 24 months of cork-liquid contact.

Absorption was determined in all the analyzed bottles by measuring the difference in weight of the cork stopper before bottling and after extraction in terms of oven-dried weight (103°C). Progression of wine on the lateral surface of each cork stopper was also determined by means of a 1 mm accuracy ruler, taking the mean of eight measurements in equidistant generatrices.

The study design was a complete factorial model with two factors (time and type of stopper) and five repetitions. Hence, the total number of measured stoppers was 40 (4 periods, 2 types, 5 repetitions). Statgraphics Centurion XV v. 15.2.00 (StatPoint Inc.) software was used for regression analyses of absorption data.

## Results and discussion

Mean values and standard deviations of absorption and progression of liquid are summarized in Table 1. As expected, both variables increased with time, reflecting the evolution of the cork-liquid interaction. Progression showed different patterns in natural and "1+1" stoppers; in the natural type, liquid progressed quickly, arising to 24 mm in three months, and oscilating between 30 mm and 25 mm until the end of the experiment. Much lower values were found for the "1+1" type at the start, probably due to the force exerted by the 6 mm natural disc on the bottle. Once this barrier was over (12 months), liquid arises to similar values as in natural type, near 25 mm after two years of contact.

Table 2 shows the results obtained for adjustments made by linear regression to the model proposed in the literature (Rosa and Fortes, 1993; Skurray *et al.* 2000b),

**Table 2.** Results obtained in regression analysis for the wine absorption model (Absorption = $a\sqrt{t}$) in both types of cork stoppers

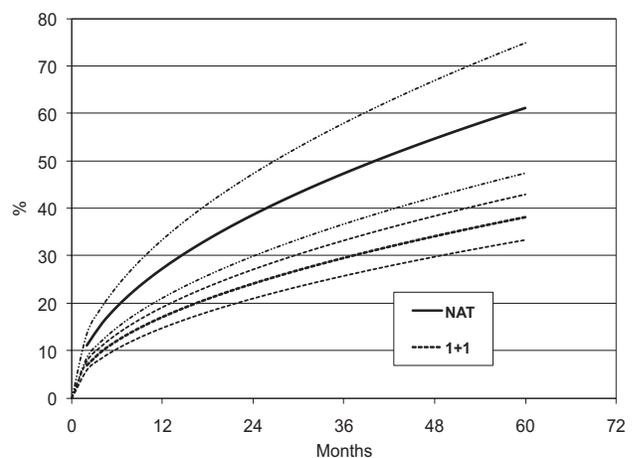|  | **Natural** | **"1+1"** |
|---|---|---|
| Coefficient ($a$) | 7.9020 | 4.9306 |
| SE | 0.844 | 0.295 |
| R-squared | 82.19 | 93.63 |
| SE of estimate | 12.66 | 4.43 |
| Mean absolute error | 9.75 | 3.48 |

SE: standard error

which is based on Fick's law, and relates absorption with time:

$$\text{Absorption} = a\sqrt{t}$$

To verify their goodness of fit, regression analyses were made with different polynomial and logarithmic models, which yielded $R^2$ values very similar to those presented (Table 2). As can be seen, the fit was better for "1+1" cork stoppers than for natural cork stoppers, which reflects the greater homogeneity of the former type of stoppers.

Figure 1 shows the regression lines estimated for wine absorption with the two types of stopper and the limits of the 95% confidence interval, extrapolated to five years of contact time. At that moment, estimated mean absorption values would be 61.2% (confidence interval 47.5% - 74.9%) for natural cork stoppers and

**Table 1.** Means (standard deviations) obtained for absorption of wine by cork stopper and liquid progression along the interface bottle – stopper

| Type of stopper | Months | Absorption (%) | Progression (mm) |
|---|---|---|---|
| Natural | 3 | 13.46 (3.41) | 24.00 (2.92) |
|  | 6 | 26.27 (15.98) | 24.00 (8.21) |
|  | 12 | 28.11 (7.84) | 30.80 (8.53) |
|  | 24 | 34.82 (18.78) | 25.00 (6.71) |
| "1 + 1" | 3 | 7.64 (1.16) | 4.31 (1.38) |
|  | 6 | 10.45 (3.02) | 5.71 (1.39) |
|  | 12 | 19.08 (5.47) | 23.63 (6.80) |
|  | 24 | 23.87 (6.58) | 24.11 (4.16) |



**Figure 1.** Prediction curves (and 95% confidence intervals) for wine absorption by cork stoppers (natural and "1+1") as a function of time.

38.2% (confidence interval 33.4% - 43.0%) for "1+1" cork stoppers.

Absorption was consistently greater in natural cork stoppers than in "1+1" stoppers, the difference tending to increase with contact time. Lower absorption by "1+1" cork stoppers is attributed to their constitution, because the liquid quickly encounters the barrier formed by the glues used to attach the disk to the agglomerate body and, within this body, to bind the cork grains together. The dif-



**Figure 2.** Scheme of different stages in the advance of the liquid fronts present in the absorption phenomenon: A) Liquid progression by cork-glass interface and diffusion in the radial direction. B) Diffusion in non-radial direction. C) After a long period of time, liquid could fill cellular lumina. $L_p$: liquid progression by the interface cork-glass; $X_d$: diffusion front; $X_f$: flow front. Colour meanings: white, empty cork cell lumina; light-brown, non-saturated cork cell walls; light purple, saturated cork cell walls; purple, liquid in the bottle, cork-glass interface and cork cell lumina.

fusion coefficient of the agglomerate is, logically, much lower than that of the natural cork, whatever the direction. The delay in lateral progression may also contribute to reduce absorption. As expected, "1+1" stoppers were much more homogeneous in both parameters.

Results make possible to study the phenomenon of wine absorption by cork stoppers thoroughly and to compare the data with those obtained in the already mentioned water absorption study (Rosa and Fortes, 1993). Figure 2 shows a scheme of the way wine goes into the stopper. For the sake of simplicity, this scheme is presented exclusively on natural type stoppers.
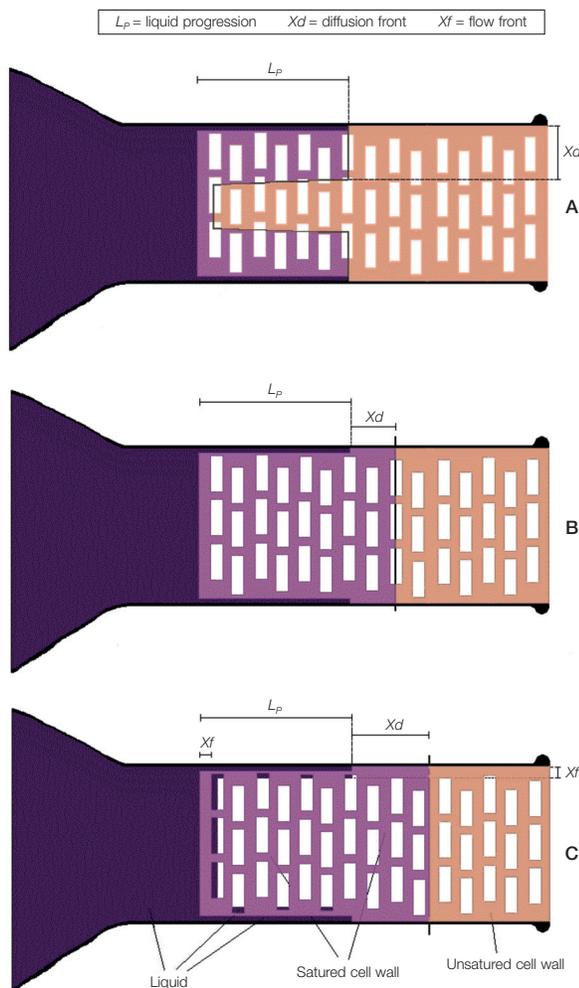
In a first stage (Figure 2A), static pressure and capillarity force liquid flow to progress along the interface cork-glass up to the point where the force exerted by the stopper against the bottle stops it ($L_p$). Surface treatment must play a key role here decreasing capillarity. Liquid will progress also through pores under this point (not shown). This is a short stage, as values are stabilized after three months contact.

Simultaneously, a diffusion front ($X_d$) moves not only from the base (non-radial direction, perpendicular to pores) but also from the lateral surfaces of the stopper (radial and non-radial direction) and the filled pores (non-radial direction). Diffusion will be faster in radial direction, and will go on until the cell wall gets saturated (absorption = 60%; Fortes *et al.,* 2004, p. 185). The radial advance of diffusion front ($Xd$) will finish when the stopper axis is reached; at this moment, all cells between the base of the stopper and the limit of liquid progression ($Lp$) are saturated. To estimate the period of time necessary to get this point, we can use the following formula derived from Fick's law (Rosa and Fortes, 1993):

$$X_d = \sqrt{\frac{4}{\pi}Dt} \qquad [1]$$

Applying as limits for radial diffusion coefficient those proposed by these authors, and $Xd = 12$ mm (stopper radium), the center of the stopper would not be reached before 2.7 months after contact. In fact, this period could be longer as surface treatment affects diffusion negatively.

Once diffusion saturates the whole body of the stopper up to the limit of liquid progression ($L_p$, Figure 2B), the front ($X_d$) will advance slowly in non-radial direction (diffusion coefficient one order of magnitude lower). In the hypothesis of all cell walls saturated under diffusion line ($L_p + X_d$ in Figure 2B) and no liquid in cell lumens after two years contact, it can be demonstrated that the distance $X_d$ may be obtained using the formula:

$$X_d = \frac{ABS \cdot L}{h_s - h_i} - L_p \qquad [2]$$

Where *ABS* is the absorption (%), *L* is the total length of the stopper (44 mm), $h_s$ is the saturation moisture content of cork (60%) and $h_i$ is the initial moisture content. Using the obtained results (estimated absorption at 24 months = 38.47%, liquid progression = 25 mm, $h_i$ = 5%) the distance covered by the liquid front absorbed by diffusion would be 5.96 mm after two years contact.

To verify these results, the non-radial diffusion coefficient can now be calculated using formula [1] with $X_d$ = 5.96 mm and *t* = 24 months; a *D* value of $4.48 \cdot 10^{-13}$ m² s⁻¹ is obtained. This coefficient is in the lower range of those proposed by the bibliography, what may be explained by the different methodologies applied, including surface treatment of specimens.

Results show a stabilization of liquid progress ($L_p$) from 3 to 24 months, and it is difficult to predict if it will remain there or not. Being a much more complex process, affected by several factors such as porosity, density, pressure or inner shape of the bottle neck, experimental data do not allow to make clear how the liquid-cork contact surface will grow with time, nor predict when the diffusion front will reach the top of the stopper. However, it may be considered that, finally, the liquid will flow filling cell lumens ($X_f$, Figure 2C). This may be due either to microcapillarity through cell wall or to evaporation-condensation phenomena (Fortes *et al.,* 2004). Estimated absorption values (from proposed model) show that liquid flow will not affect to more than a few layers of cells in the outer side of the stopper after five years of contact.

It may be concluded that absorption behavior of the two types of cork stopper differed significantly. "1+1" cork stoppers absorbed less liquid than natural cork stoppers and lateral progression was smaller. The data obtained make it possible to assess the relative importance of the two phenomena associated to liquid absorption by the cork stopper: diffusion and liquid flow. According to the well known impermeability of cork, liquid flow through cork stoppers has a very small weight in the absorption process. On the opposite, liquid progression by the cork-glass interface and diffusion through cell walls are responsible for the evolution of the absorption process. Results highlight the key paper of surface treatment and mechanical behaviour on absorption, conditioning lateral progress of liquid by the cork-glass interface and diffusion coefficient in the stopper.

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