CORK-WINE INTERACTION STUDIES: LIQUID ABSORPTION AND NON-VOLATILE COMPOUND MIGRATION

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Abstract

Aims: To provide a better knowledge of cork-wine interaction, focussing on absorption of liquid by the cork stopper and overall migration of non-volatile compounds from the cork-stopper to liquid.

Methods and results: Natural cork stoppers and 1+1 technical cork stoppers (agglomerate cork body ended with natural cork washers), with and without surface treatment, were used to close bottles filled with 12 % v/v ethanolic solution and removed after 3, 6, 12 and 24 months of contact. Mean and limit values of absorption and overall migration at each time are used to compare treated and non-treated stoppers. Variation of absorption with contact time was studied by adjusting the ABSORPTION = a · √t model (R^2: 0.8572 - 0.9756).

Conclusion: Most of the overall migration is due to natural components of cork. Contact time and type of cork stopper are the factors responsible for the greatest variability. Surface treatment increases overall migration (2 mg/stopper) and reduces liquid absorption (more than 10 %).

Significance and impact of the study: The results show how a correct characterization of stopper and surface treatment is needed to predict the evolution of cork-wine interaction.

Key words: cork stopper, cork-wine interaction, absorption, overall migration, surface treatment

Résumé

Objectif : Fournir une meilleure connaissance de l'interaction du bouchon-vin, visant sur l'absorption de liquide par le bouchon et la migration de composés non-volatils du bouchon au liquide.

Méthodes and résultats : Des bouchons naturels et des bouchons 1+1 techniques (comprenant un manche en liège aggloméré et une rondelle en liège naturel collée sur les deux bouts), avec et sans traitement de la surface, ont été utilisés pour fermer des bouteilles contenant une solution hydroalcoolique de12 % (v/v) et ont été otés après 3, 6, 12 et 24 mois de contact. Les valeurs moyennes et limites de l'absorption et la migration totale à chaque temps (de contact) ont été utilisées pour comparer les bouchons traités et les non-traités. La variation de l'absorption avec le temps de contact a été étudiée en ajustant l'équation ABSORPTION = a · √t (R^2: 0,8572 - 0,9756).

Conclusion : La plupart de la migration totale est due aux composants naturels du liège. Le temps de contact et le type de bouchon sont les facteurs responsables de la plus grande variabilité. Le traitement de la surface augmente la migration totale (2 mg/bouchon) et réduit l'absorption de liquide (plus de 10 %).

Signification et impact de l'étude : Les résultats montrent comment une bonne caractérisation du bouchon et du traitement de la surface est nécessaire pour prédire l'évolution de l'interaction bouchon-vin.

Mots-clés : bouchon en liège, interaction bouchon-vin, absorption, traitement de la surface

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INTRODUCTION

Cork is used in enology due to various physical-mechanical and chemical properties of the material, including impermeability, mechanical behavior and chemical inertia. 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 notable, 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 focused on two less studied aspects: absorption of liquids by the cork stopper and migration of non-volatile compounds from stopper to wine.

The interest in the absorption phenomenon is due to the fact that it notably alters the behavior and properties of cork, a hygroscopic material. From a physical-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; and, on the other, increased moisture content diminishes pressure against the glass, an effect which is added to 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).

The main physical phenomenon related with absorption is diffusion of fluid through cork, 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 that is regulated by Fick's law, which represents the relation between flow and the gradient of concentration (moisture) 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} $m^2 \cdot s^{-1}$) (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.*, 2000), 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 disk-ended technical cork stoppers (1+1 type, with an agglomerate cork body and a washer of natural corkwood glued on both ends) both directions are parallel. Recent studies on samples with very low moisture content (3.5 %) yield D coefficient values one or two orders of magnitude lower (10^{-13} $m^2 \cdot s^{-1}$) than those cited (Marat-Mendes and Neagu, 2004; Marat-Mendes and Neagu, 2003)

With regard to overall migration, it's to be highlighted that cork has, in addition to volatile compounds, non-volatile components that are not chemically bound to the primary structure and are thus extractable with solvents. These components, commonly called extractive components, comprise mainly waxes, triterpenes and phenol compounds, and may account for up to 18 % of total cork weight (Pereira, 2007). Some of these phenol compounds (ellagitannins as castalagin, grandinin and vescalagin, and low molecular weight polyphenols as ellagic and gallic acid and vainillin) are also present in oak wood and are responsible for some of the sensory properties of wine (Varea *et al.*, 2001; Fernández de Simón *et al.*, 1999; Mazzoleni *et al.*, 1998; Fernández de Simón *et al.*, 1996). In any case, the extraction and migration of these compounds is an extremely slow process, since the absorption by wine is hindered by the impermeability of the material. Interest in these compounds has increased notably in recent years due to their beneficial effects on health (Pereira, 2007).

At the same time, the cork-wine interaction is altered by the finishing processes to which the cork stopper is subjected, especially washing and, particularly, surface treatment. This operation consists in coating the surface of the cork stopper with a thin layer (≈50 µ) of silicone (and, in some cases, paraffin), which reduces the coefficient of friction, increases the impermeability of the cork stopper, and improves the seal of the surface between cork and glass (Fortes *et al.*, 2004; Fugelsang *et al.*, 1997). The potential migration of these compounds into the wine has been studied and possible health risks have been excluded (Six and Feigenbaum, 2003; Six *et al.*, 2002).

Scarce literature is found on these subjects, which makes important to characterize the evolution in time of the cork-liquid interaction by measuring the amount of liquid retained by the cork (absorption) and the total amount of non-volatile compounds yielded by the cork stopper into ethanol solution (overall migration). This study was undertaken to evaluate the magnitude of both phenomena under conditions as close to real conditions as possible, to study their evolution in time, and to analyze the influence of the various factors described (type of cork stopper and finishing processes).

MATERIALS AND METHODS

1. Cork stoppers

Two types of cork stoppers were used: natural (first quality) and 1+1 technical (with an agglomerate cork body and a washer of natural corkwood glued on both ends). As discussed above, the direction of progression of liquid is perpendicular to the pores in natural cork stoppers, whereas it is parallel to the pores in 1+1 technical cork stoppers.

All cork stoppers were rinsed in water in a rotating drum (untreated stoppers). Next, half of the stoppers of each type were subjected to the most common industrial finishing process: washing with hydrogen peroxide followed by surface application of an aqueous emulsion of paraffin and silicone (a mixture of polydimethylsiloxane, inert fillers, food-grade pigments, paraffin and teflon) (treated stoppers).

2. Experimental design, bottling and storage

Burgundy bottles (375-ml capacity) were filled in the laboratory with a 12 % ethanol (V/V) solution. The filling level was verified, and bottles were sealed using an automatic bottling machine. The study design was a complete factorial model with three factors and 15 repetitions.

All bottles had a CETIE neck with standardized inner dimensions (UNE-EN 12726 standard). Cork stoppers were conditioned to 20 °C and 65 % RH and weighed before bottling. After bottling, bottles were left standing for 24 h and then were laid down and stored in this position at 16°C ± 2 °C and 55 % ± 15 % RH until the cork stopper was removed. Measurements were made after 3, 6, 12 and 24 months of cork-liquid contact.

3. Measurement of absorption, progression and overall migration

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).

Overall migration was measured using 9 of the 15 repetitions; the liquid from three bottles (1.125 l) was mixed for each determination. The mixture was dried by eliminating the wine simulant in a rotary evaporator and drying the residue in a 103 °C oven. Overall migration is the weight of the dry residue per stopper.

4. Statistical analysis

Absorption and overall migration were assessed by univariate variance analysis using a complete factorial model and cork stopper type, surface treatment and contact time as fixed factors. The absorption data were processed using linear regression analysis, adjusting a model based on the one proposed in the literature (Skurray *et al.*, 2000; Rosa and Fortes, 1993). Version 13.0.1 of the SPSS for Windows (SPSS Inc.) statistical program was used for analysis of variance and Statgraphics Centurion XV V 15.2.00 (StatPoint Inc.) for regression analyses.

RESULTS AND DISCUSSION

Mean values of absorption and overall migration are summarized in table 1 and figures 1 and 2. As expected, studied variables increased with time, reflecting the evolution of the cork-liquid interaction.

Table 1 - Means (standard deviations) obtained for the variables studied

		Months	Absorption (%)	Overall migration (mg/stopper)
NAT	not treated	3	23.83 (11.51)	0.97 (0.44)
		6	29.53 (11.75)	1.94 (0.85)
		12	34.05 (8.44)	2.72 (0.22)
		24	52.53 (11.96)	2.49 (0.13)
	treated	3	8.64 (2.82)	3.60 (1.44)
		6	13.29 (6.28)	2.92 (0.55)
		12	19.34 (5.61)	4.57 (0.40)
		24	26.79 (12.61)	5.08 (1.13)
1+1	not treated	3	14.69 (1.58)	2.91 (0.31)
		6	22.95 (2.90)	4.68 (0.25)
		12	27.76 (3.07)	6.82 (0.55)
		24	36.46 (5.74)	12.76 (1.30)
	treated	3	8.58 (2.32)	5.08 (2.03)
		6	10.33 (2.79)	5.90 (0.66)
		12	12.96 (3.10)	9.30 (1.33)
		24	19.04 (4.28)	15.64 (4.89)

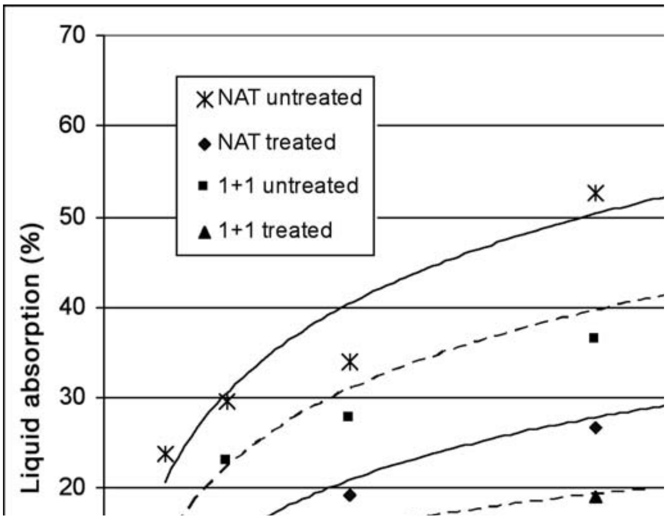

Figure 1 - Evolution of liquid absorption with time. Continue lines (--) show trends (logarithmic model) for natural cork stoppers (NAT) while dashed lines (----) show trends for technical stoppers (1+1).

The results of variance analysis are summarized in table 2. As it can be seen, the proposed model explains the phenomenon of overall migration very well (adjusted $R^2 = 0.863$); in absorption, the variance attributed to the model is smaller. The three studied factors (type of cork stopper, surface treatment and contact time) showed significant effects ($Pr < 0.001$) for both variables. Interactions between factors generally were not significant, although there were some exceptions that will be discussed below.

Absorption results and corresponding trend lines are shown in figure 1, clearly reflecting the effect of surface treatment (the factor with highest weight for this variable - table 2) and type of stopper. Differences in absorption between treated and untreated cork stoppers were greater than 12 % in every case except 1+1 technical stoppers at 3 months. Type of cork stopper has a minor but significant effect, absorption being consistently greater in natural cork stoppers than in 1+1 technical stoppers, and the difference tending to increase with contact time. Lower absorption by 1+1 technical 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 diffusion coefficient of the agglomerate is, logically, much lower than that of the natural cork, whatever the direction.

As mentioned in the introduction, absorption is particularly important because of its influence on the behavior of the stopper. To better understand the evolution of this parameter with contact time, various adjustments were made by linear regression to the model proposed in the literature (Skurray *et al.*, 2000; Rosa and Fortes, 1993), which is based on Fick's law:

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

Results are shown in table 3. To verify their goodness of fit, regression analyses were made with different types of models (polynomial and logarithmic), which yielded R^2 values very similar to those presented.

As it can be seen, the fit was notably better for 1+1 technical cork stoppers than for natural cork stoppers, which reflects the greater homogeneity of the former type of stoppers. Comparisons between models for treated and untreated stoppers showed lower R^2 when treatment was included. One interpretation could be that the presence of the silicone and paraffin barrier increased the variability of absorption, perhaps due to a lack of homogeneity in the treatment applied.

Table 2 - Results of tests of inter-subject effects for absorption (%) and overall migration (mg/stopper)

	Absorption			Overall migration		
Source	Sum of squares	Df	Pr	Sum of squares	Df	Pr
Corrected model (a)	31,804.4	15	0.000	721.9	15	0.000
Intersection	122,016.8	1	0.000	1,431.9	1	0.000
Type of stopper	2,861.2	1	0.000	282.2	1	0.000
Time	12,720.5	3	0.000	246.8	3	0.000
Treatment	14,145.9	1	0.000	53.0	1	0.000
Type * Time	528.7	3	0.017	134.9	3	0.000
Type * Treatment	410.0	1	0.005	0.1	1	0.845
Time * Treatment	931.2	3	0.001	4.5	3	0.591
Type * Time * Treatment	206.9	3	0.259	0.5	3	0.977
Error	11,439.3	224		74.4	32	
Total	165,260.6	240		2,228.1	48	
Corrected total	43,243.8	239		796.2	47	
(a) R^2	0.735			0.907		
(a) Adjusted R^2	0.718			0.863		

Table 3 - Results of fitting a linear regression model for liquid absorption (ABS, %) by cork stoppers as a function of time (t, weeks) using the equation ABS = a · √t

	Natural		1+1	
	untreated	treated	untreated	treated
Coefficient (a)	5.3039	2.6644	3.8638	1.9340
Standard error	0.2105	0.1415	0.0795	0.0613
R^2	0.9149	0.8573	0.9756	0.9440
SE of estimate	11.21	7.54	4.24	3.27
Mean absolute error	8.52	5.41	3.04	2.68

The high correlation coefficient obtained for overall migration indicates that the model accounts for almost all the existing variance (table 2). The factor with the greatest weight in this case was the type of cork stopper, followed by contact time; surface treatment had a smaller, but significant, effect that was independent of the type of cork stopper and contact time. Only the interaction between type of cork stopper and contact time was significant, due to differences in the evolution of overall migration in both types of cork stopper. This interaction can also be observed in figure 2: overall migration exhibited a small increase with time in natural cork stoppers, with values close to the initial values after 24 months of contact; in contrast, the overall migration values of the 1+1 technical cork stoppers were 3 to 4 times greater than the initial values (table 1, figure 1). The differences between the two types of stoppers must be attributed to differences in pore disposition and in chemical composition of the cell wall of cork and of the tissue filling and lining the lenticels.

Moreover, the fact that the cork stoppers were subjected to a finishing process (washing and surface treatment) implied an increase in overall migration of approximately 2 mg/stopper, which was consistent for both types of cork stopper, whatever the period of time considered. To understand exactly why this increase occurs, it would be necessary to analyze the chemical composition of the residue, which was beyond the scope of the study. In principle, two hypotheses can be formulated, which both may be simultaneously valid: that the surface treatment products transfer part of their components to the wine or that the washing processes slightly modify the chemical structure of the tissue, thus facilitating the extraction of compounds.

In any case, the overall migration values shown in table 1 are low, much lower than the maximum allowed by European regulations -60 mg/stopper, according to Council of Europe resolution ResAP(2004)2-. In individual tests, the maximum values obtained were 20.20 and 6.18 mg/stopper for 1+1 technical and natural cork stoppers, respectively; both maximum values were obtained in treated stoppers. Most of this migration comes from the natural compounds of cork, which would be that of cork stoppers that have not received surface treatment (see figure 2, table 1). These compounds are mainly polyphenols (ellagitannins and phenolic acids and aldehydes) very similar to those of oak wood, as indicated before (Varea *et al.*, 2001). Thus, contact with the cork stopper presumably results in a small but significant transfer of substances that can influence the sensory properties of wine, completing the barrel maturation process in the bottle.

CONCLUSIONS

The results obtained reveal the complexity of the cork-liquid interaction phenomenon, which is affected by the three factors studied (contact time, type of cork stopper and surface treatment). The model proposed for analysis of variance provides good results in the case of overall migration, although the percentage of variability explained diminishes for absorption.

The behavior of the two types of cork stopper used differed significantly. Technical cork stoppers (1+1) absorbed less liquid than natural cork stoppers but they produced more overall migration from six months on. In any case, the amount of non-volatile compounds that

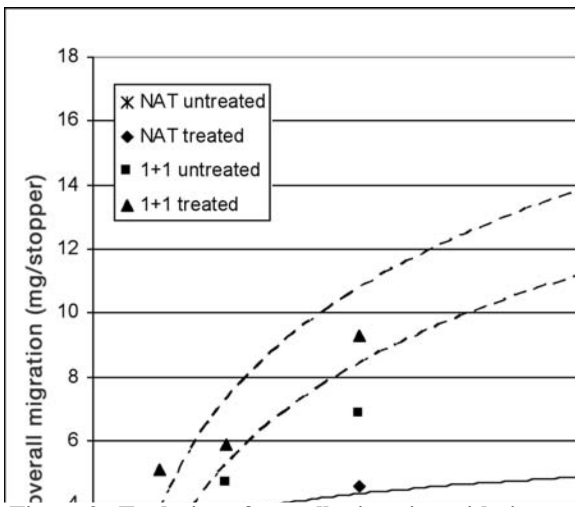

Figure 2 - Evolution of overall migration with time. Continue lines (--) show trends (logarithmic model) for natural cork stoppers (NAT) while dashed lines (----) show trends for technical stoppers (1+1).

migrated from the cork stopper into the wine was much lower than the limits established by European standards.

Surface treatment reduced absorption (differences between treated and untreated stoppers ranging from 6,12 to 25,74 %), and produced a relatively small increase in overall migration, around 2 mg/stopper, an amount that seemed to remain constant and independent of the type of cork stopper and contact time.

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