Cork closures
Impact on the quality of bottled wines

Paulo Lopes
Enologist PhD (Faculté d'Œnologie de Bordeaux)
WineMBA (BEM, UC Davis, UniSA)

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Impact of closures on wine quality

**Intrinsic wine attributes**
Impact on aroma, taste, color

**Extrinsic wine attributes**
Quality perceived by the consumers

**Sustainability**
How corks can influence wine quality after bottling

- Gas barrier properties
- TCA
- Intrinsic wine attributes
- Chemical composition
Main mechanism of TCA formation

Lignine

Organ chorine products
- Pesticides, Flame retardants
- Wood treatment

Biodegradation
PCP/lindane

Sugars

Molds

Phenol

ClO\(^-\)

2,4,6 – trichlorophenol (TCP)

Biomethylation
Trichoderma, Fusarium, Penicillium…
(Alvarez-Rodriguez et al., 2003)

2,4,6 – trichloroanisole (TCA)
Amorim’s strategy anti-TCA

TCA in cork

Prevention
- Traceability
- Storage conditions
- Stringent control of cork
- Boiling systems
- Chlorine removal

Cure
- ROSA®
- ROSA Evolution®
- Vaporisation

Quality control
- GC analysis
- Sensory analysis
Prevention

Prevent TCA formation during cork stopper manufacture

Cork lots traceability

Removal of “calços” (10 cm)
Exclusion of yellow stain cork planks

Boiling system that reduces cork storage

Chlorine exclusion
Descontamination

Steam distillation treatments

ROSA®
Patent nº PT103910
Cork granules
-80 to 90% of TCA

ROSA Evolution®
Patent nº PT103910
Natural cork stoppers
-80% of TCA

Vaporization
Cork planks
-40% of TCA

- 80.3%
- 69 to 72%
- 80%
- 75%

ROSA®
Patent nº PT103910

ROSA Evolution®
Patent nº PT103910

Vaporization
Cork planks
-40% of TCA
Mechanism of TCA migration from cork into wine

Wine contamination occurs by direct contact with cork contaminated surfaces.
Quality control

**GC and sensory analysis**

**GC/MS/ECD-SPME** (LD = 0.3 ng/L et LQ = 0.5 ng/L)

13 GCs split by the raw material, cork and R&D* Units

> 15000 samples per month*
Strategy results

Internal

Natural corks

Champagne

Neutrocork
Strategy results

External

The CQC cork sampling program is rigorous. For a typical lot of 100,000 corks CQC guidelines require a minimum sample of 250 corks taken from a selection of at least five separate bales. These corks are placed in 50-cork wine soaks for 24 hours to extract releasable TCA. Resulting soaks are analyzed at ETS Laboratories using a method that reports TCA at concentrations as low as 1 part per trillion. If one of the five soaks indicates TCA as high as 1.5ppt - the entire cork lot is flagged and withheld from inventory.
Closures barrier properties

Impact on wine quality after bottling
Measurement of O\textsubscript{2} transfer through closures

Colorimetry: Indicator of oxidation-reduction (Indigo carmine)

Kinetics of oxygen ingress through different closures

Oxygen ingresses through closures independently of storage position

Main routes by which $O_2$ enters into bottles

Total $O_2$ into wine bottle after bottling

1) Dissolved oxygen in wine

2) Gaseous oxygen in the bottle headspace

3) Oxygen within the closure

4) Oxygen that enters throughout the closure

Wine exposition to oxygen before and during bottling are very important, their effect (cumulative) can be only observed during post-bottling.
Sealing effectiveness of closures to volatile compounds

Storage under contaminated environment

- Microagglomerate cork
- Natural cork
- Nomacorc light
- Nomacorc premium
- Screw cap saranex

\( d_5 \)-TCA: 1,75 µg/L\(_{\text{air}} \)
\( d_4 \)-E4P: 1,73 mg/L\(_{\text{air}} \)
\( d_4 \)-E4G: 0,15 mg/L\(_{\text{air}} \)

1.12 and 30 months of Storage
Sealing effectiveness of closures to volatile compounds

Cork is an effective barrier!!! TCA does not migrate through cork after bottling.

Impact of bottling and closure OTR on the chemical & sensory properties of a Sauvignon blanc

<table>
<thead>
<tr>
<th>Vin</th>
<th>100% Sauvignon blanc; Côte du Duras 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>TAV 12,2%</td>
</tr>
<tr>
<td></td>
<td>Volatile acidity 0,29 g/l H₂SO₄</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bottles</th>
<th>Bordelaise Tradition CETIE</th>
<th>Bordelaise BVS 30H60</th>
<th>Ampole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closures</td>
<td>Natural cork</td>
<td>Colmated cork</td>
<td>Agglomerate</td>
</tr>
<tr>
<td>Analyses</td>
<td>Free SO₂</td>
<td>Total SO₂</td>
<td>Ascorbic acid</td>
</tr>
</tbody>
</table>

Analyses after 2, 12 and 24 months
Impact of bottling and closure OTR on the chemical & sensory properties of a Sauvignon blanc

Significant variation on O$_2$ dissolved during bottling

![Graph showing dissolved O$_2$ levels during bottling runs with different closures.](image-url)
Impact of bottling and closure OTR on the chemical & sensory properties of a Sauvignon blanc

Ascorbic acid and free SO$_2$

Impact of bottling and closure OTR on the chemical & sensory properties of a Sauvignon blanc

Ascorbic acid and free SO$_2$
Impact of bottling and closure OTR on the chemical & sensory properties of a Sauvignon blanc

**Varietal thiols (3MH & 4MMP)**

**3-mercaptohexan-1-ol (3MH)**
- Passion fruit, grapefruit

**4-mercapto-4-methylpentan-2-one (4MMP)**
- Broom

![Graph showing concentrations of 3MH and 4MMP for different closures.](image-url)
Impact of bottling and closure OTR on the chemical & sensory properties of a Sauvignon blanc

Reductive (H$_2$S) and oxidative (Sotolon) characters

![Graph showing impact of bottling and closure OTR on H$_2$S and Sotolon concentrations](image)
Impact of bottling and closure OTR on the chemical & sensory properties of a Sauvignon blanc

Compositional & sensory at 24 months

# Impact of bottling and closure OTR on the chemical & sensory properties of a Merlot

<table>
<thead>
<tr>
<th>Vin</th>
<th>100% Merlot 2002, UDP Saint Emilion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td></td>
</tr>
<tr>
<td>TAV</td>
<td>12.4%</td>
</tr>
<tr>
<td>Volatile acidity</td>
<td>0.37 g/l H₂SO₄</td>
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<tr>
<td><strong>Bottles</strong></td>
<td>Bordelaise Tradition</td>
</tr>
<tr>
<td><strong>Closures</strong></td>
<td>Natural cork</td>
</tr>
<tr>
<td><strong>Analyses</strong></td>
<td>Free SO₂</td>
</tr>
</tbody>
</table>

Analyses after 6, 12 and 20 months
Impact of bottling and closure OTR on the chemical & sensory properties of a Merlot

Chemical evolution during 20 months of storage

Factor 1: 53.61%
Factor 2: 10.34%

Free anthocyanins
TA+
A-vinyl-T
Pyranoanthocyanins
% Polymerized anthocyanins
Phenolic acids
Flavanols
Flavonols
Tannins
DPm
Total SO2
Free SO2
Acetaldehyde
IC'
d420%
d520%
d620%
A-ethyl-T
Hue

T0
6 months
12 months
20 months

- Control
- Cork “flor”
- Colmated
- Agglomerate
- 1+1
- Microagglomerate
- Nomacorc classic
- Sc saran-tin
- SC saranex

Chemical evolution during 20 months of storage
Impact of bottling and closure OTR on the chemical & sensory properties of a Merlot

Sensory assessment at 36 months

Metal catalysed wine oxidation mechanism

O₂ → HOO⁻ → HOOH → HO⁻

Fe²⁺ → Fe³⁺

Hydroperoxyl radical

Hydrogen peroxide

Hydroxyl radical

1-hydroxyethyl radical

Acetaldehyde

Malvidin-3-glucoside

Flavanol

Color stabilisation

Bisulfite

Sulfuric acid

Scavenge thiols (nucleophilic compounds)

Aroma loss
Possible post-bottling reduction mechanism

- **Sulfites**
- **Pesticides**
- **Sulfate**
- **SO₂**
- **Inorganic sulfur**

**Sulfur containing amino acids**

**Metal Catalyzed**

- **Catechol**
  - **Quinone**
  - **Semiquinone**

**Ethanol**

- **CH₃CH₂OH**

**Ethanethiol**

- **CH₃CH₂SH**

**Aroma**

- Rotten egg, sewage like aroma
- Onion, rubbery, burnt match aroma
Chemical composition of cork

**Structural fraction**
- 45% suberin
- 27% lignin
- 12% polysaccharides

**Extractible fraction**
- 6% Triterpenes
- 6% phenolic compounds
- 1% minerals
Chemical composition of cork

**Phenolic compounds**

**Phenolic acids and aldehydes**

- m/z 151 (vanilin)
- m/z 169 (Gallic acid)
- m/z 153 (Protocatechuic acid)
- m/z 179 (Caffeic acid)
- m/z 137 (Protocatechuic aldehyde)
- m/z 177 (Coneyferaldehyde)

**Gallic and Ellagic acid derivates**

- m/z 301 (Ellagic acid)
- m/z 469 (Valonic acid dilactone)
- m/z 505 (Valonic acid)

**Ellagictannins**

- m/z 933 (Vescalagin/castalagin)
- m/z 935 (di-HHD-glucosyl-galloyl-glucose)
- m/z 939 (Pentagalloyl-glucose)
- m/z 783 (di-HHD-glucose)
- m/z 1135 (Mongolicain)

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FERNANDES, A., MATEUS, N., CABRAL, M.; FREITAS, V. 2011. Analysis of phenolic compounds in cork from Quercus suber L. by HPLC-DAD/ESI-MS. Food Chemistry 125, 1398-1405
Chemical composition of cork

Migration of phenolic compounds from cork into bottled solutions

On going study for 36 months (30°C)
Natural cork “Flor” grade with and without surface treatment
Natural cork grade 3 with and without surface treatment

Very small amounts of phenolic compounds migrate into wine
The amounts observed phenolic do not impact the wine sensory properties…but do they can contribute to the modulation of oxidative reductive reactions???
Metal catalysed wine oxidation mechanism

Phenolic compounds have a key role on wine bottle ageing
Intrinsic wine attributes
Impact on aroma, taste, color

Extrinsic wine attributes
Quality perceived by the consumers

Sustainability
Importance of extrinsic wine attributes on the consumer

Wine (red, white, rosé)
Wine variety
Promotion
Brand
Country
Region
Price
Alcohol level
Year
Medals
Green credentials: logo
Packaging:
  Type of closure
  Type of capsule
  Bottle: volume, type, color
  Label: style, type, color
  …
Importance of extrinsic wine attributes for Canadians purchase

<table>
<thead>
<tr>
<th>Attributes</th>
<th>Ontario (n=298)</th>
<th>Québec (n=299)</th>
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</thead>
<tbody>
<tr>
<td>Price</td>
<td>5.5</td>
<td>5.2</td>
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<tr>
<td>Label information</td>
<td>4.7</td>
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<tr>
<td>Alcohol level</td>
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<tr>
<td>Country of origin</td>
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<tr>
<td>Grape variety</td>
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<td>Brand name</td>
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<td>Type of closure</td>
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<td>Capsule material</td>
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<td>Label pictures</td>
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<td>Bottle weight</td>
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<td>Label material</td>
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<tr>
<td>Bottle shape</td>
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</tbody>
</table>

Values represent mean values based upon 7 likert scale with 7 = very important, 4 = neutral, 1 = unimportant. Same color within the each column indicates homogenous statistical groups at 95% confidence level.
Consumers attitudes towards wine closures

- On-line survey
- 597 wine consumers (Ontario; n= 298; Québec, n = 299)
- Technique: Traditional Conjoint Analysis
- 12 graphical representations with the following scenario:
  « Purchase in retail of an eco-labeled wine to drink by themselves or with other people at home

- Questions:
  - Likelihood of buying this bottle (juster scale)
  - price
  - Realistically intention of purchase (yes/no)

Wine sealed with natural corks enjoys a pricing advantage of CAD$1.69 and CAD$1.39 per bottle when compared with screw caps and synthetic.
Key findings

- TCA is under control; however, there is some room to improvement
- Gas barrier properties of cork closures are unique, providing an effective barrier against exogenous compounds and releasing low amounts of oxygen that provide a well-balanced wine development
- Wine development after bottling seems to be rather reductive than oxidative; operations and closures that provide a high and continuous oxygenation are detrimental to wine quality!
- Phenolic compounds migrate from cork into wine; can they participate on the wine oxidative-reductive reactions ???
- Natural cork ingrains itself in the minds of consumers as the status quo, while screw caps and synthetic introduce a cognitive dissonance, create poor brand image and thus negative influence the purchase and price
Thanks very much!!!!

Questions, critics, comments

LinkedIn: Paulo Lopes