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Report

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Your project

Molecular analyses on wines closed with and without cork coated with Procork Membrane

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REPORT SUMMARY

1 Introduction and purpose

The Procork company developed a membrane technology to control the rate of oxygen entering the wine bottles when closed with natural cork. This membrane made of 5 different layers allows selective permeation of oxygen to allow micro-aeration of grape and oak barrel tannins while blocking compounds passing from the cork to the wine.

A triangular sensory test has already been conducted by Sensenet using synthetic wines, to confirm the inertness and food neutrality of the Procork membrane. The triangle test compared a synthetic wine which has been in contact with the membrane and the “control” synthetic wine and confirmed the inertness of the ProCork membrane.

To further investigate the impact of the membrane on wine, two bottles of Chablis 1er cru, Fourchaume, [redacted] 2018 have been compared: one closed with [redacted] technical cork, the other closed with a cork coated with the Procork membrane.

Those two bottles have been tasted in February and April 2020 by the independent Bordeaux based wine critic Jean Marc Quarin. The Procork bottle has been described as having a more ripe fruit character than the [redacted]e.

To deepen the comparison of those two bottles, Sensenet performed molecular analyses (GC-TofMS) on the headspace of the two wine bottles. Those molecular analyses helped to understand the evolution in volatile organic compounds composition between the two bottles.

This document summarizes the results obtained after GC-TofMS molecular analyses. Results analysis focuses on the major sensory difference highlighted by the professional taster, Mr. Quarin.

2 Services summary

Title: Molecular analyses on wines closed with and without cork coated with Procork membrane		
Experimental Plan		
Number of samples	Two bottles of the same wine: - 1 closed with cork coated with the Procork membrane - 1 closed with [redacted] technical cork	
Sampling		
Protocol	The wine was introduced into a micro-chamber (at 27 °C. for 10 minutes), the headspace was then trapped on Tenax® tubes by helium scanning.	
Analyses		
Molecular analyses		
Parameters	**Methodologies**	**Details**
GC-TofMS	• Thermal desorption platform Unity2, Markes International • Gaz chromatograph Agilent 7890A Mass spectrometer BenchTOF-dx ALMSCO	Detection, identification et semi-quantification of all compounds. Concentration comparison to compound theoretical odour threshold value if available.

3 Experimental

3.1 Wine bottles tested

The wine used for this study was a white wine: a Chablis 1er cru, Fourchaume, [redacted] 2018.

Two different bottles were used: one closed with [redacted] technical cork and the second closed with a cork coated with the Procork membrane. Those two wine bottles have been stored in the same conditions for six months.

3.2 Headspace extraction sampling protocol for volatile organic compounds composition analysis

The headspace of each wine was sampled using an individual Microchamber (M-CTE250, Markes Int) heated at 27°C, to mimic the temperature the wine can reach when placed in contact with the palate. Indeed, during wine degustation some volatile compounds volatilize only when placed in the mouth due to their boiling point.

A defined quantity of wine (40mL) was introduced and confined in the microchamber. To collect samples, an absorbent tube (Tenax/Sulphicarb) was inserted on the top of the microchamber. A total of 1000 mL of headspace volume was collected during 10 minutes. To promote the transport of the volatile organic compounds from the headspace to the tube a nitrogen gas a flow of 10 mL/min (99.999% purity N2) was used. An additional tube, without sample, was prepared in the same sampling conditions as a blank. The sampling was made in duplicate (2 tubes for each sample). The sample tubes were kept closed with two plugs at their ends until the time of analysis.

Initial wine sampling was performed just after removing the cork from the bottle to avoid any additional oxidation due to contact of the wine with the air.

3.3 Molecular Analyses

Our instrument is composed of a gas chromatograph (Agilent 7890 model, US), Time-of-Flight mass spectrometer (BenchTOF-dx model, Almsco, Germany) and thermal desorption unity (Unity2, Markes, UK).

The desorption Tenax® tubes were connected to the thermodesorption unit of the GC-ToFMS instrument. They were individually subjected to high temperatures during an initial phase to desorb the VOC captured during sampling. Afterwards, VOCs were entrained by a flow of helium carrier gas (99.9999% purity He) to a cold trap at low temperature by thermoelectric cooling, where they were again retained. Then, the cold trap was heated drastically to release and drag all VOCs into the GC for subsequent chromatographic separation. At the end of the tour of the GC column, once separated, the compounds reached the mass detector at different times, being ionized and by the Time-of-Flight (ToF) selector. The TargetView V3 software (ALMSCO, Germany) has been used to carry out deconvolution process providing the chemical identification from the GC-MS data.

Due to the high amounts of alcohols and esters leading to coelution phenomenon between the peaks, the analysis and processing of the samples was made three times using different analysis conditions.

4 Results and discussion

4.1 Volatile organic compounds composition comparison

GC-TofMS analyses have been performed on the samples collected on the two wine bottles. The table on next page presents the main results of the analyses by GC-TofMS (identification and quantification of the volatile organic compounds present). Compounds present in quantities greater than their theoretical olfactory threshold (OTV) or in notable concentrations as well as totals by chemical families are summarized here. Full results are provided in ANNEX 1.

A comparison of the measured concentrations with the olfactory thresholds of the compounds (OTV) (if available) is proposed. This theoretical OTV corresponds to the mass of compound that can just be perceived when evaporated in a cubic meter of neutral air. An order of the number of times by which the measured concentration is greater than the theoretical olfactory threshold (OTV) is indicated. The colour coding below helps to understand the potential participation of the compound to the overall product odour.

COLOUR CODE:

<1 x Theoretical olfactory threshold (OTV)
1-10 x Theoretical olfactory threshold (OTV)
10-50 x Theoretical olfactory threshold (OTV)
50-100 x Theoretical olfactory threshold (OTV)
100-1000 x Theoretical olfactory threshold (OTV)
>1000 x Theoretical olfactory threshold (OTV)

GC-TOFMS MAIN RESULTS

Compound	CAS No.	Concentration (ug/m^3) [redacted] Bottle	Procork bottle	OTV available?
Alcohols				
1-Propanol	71-23-8	**12 783,1**	**19 946,2**	yes
1-Propanol, 2-methyl-	78-83-1	**17 533,5**	**16 445,8**	yes
1-Butanol	71-36-3	**1 029,6**	**938,7**	yes
1-Butanol, 3-methyl-	123-51-3	**77 522,2**	**70 255,5**	yes
1-Butanol, 2-methyl-	137-32-6	**24 536,0**	**23 980,2**	yes
1-Hexanol	111-27-3	**637,2**	**717,6**	yes
	Total Alcohols	**135 105,2**	**133 245,3**	
Aldehydes				
Acetaldehyde (*)	75-07-0	**1 491,7**	**1 473,3**	yes
Propanal, 2-methyl-	78-84-2	**16,5**	**56,7**	yes
Methacrolein	78-85-3	**52,4**	**36,9**	yes
Butanal, 3-methyl-	590-86-3	**730,1**	**1 411,9**	yes
Benzaldehyde	100-52-7	**2,3**	**2,0**	yes
	Total Aldehydes	**2 325,6**	**3 065,0**	
Aromatic compounds				
	Total Aromatic compounds	**2,2**	**14,7**	
Cyclic Hydrocarbons				
	Total Cyclic Hydrocarbons	**2,6**	**0,0**	
Esters				
Ethyl Acetate	141-78-6	**75 095,4**	**67 436,3**	yes
Propanoic acid, ethyl ester	105-37-3	**2 614,2**	**2 365,8**	yes
Propanoic acid, 2-methyl-, ethyl ester	97-62-1	**593,3**	**600,5**	yes
Isobutyl acetate	110-19-0	**243,5**	**102,6**	yes
Butanoic acid, ethyl ester	105-54-4	**3 271,7**	**2 989,8**	yes
Butanoic acid, 3-methyl-, ethyl ester	108-64-5	**180,2**	**190,9**	yes
1-Butanol, 3-methyl-, acetate	123-92-2	**7 952,1**	**6 702,0**	yes
1-Butanol, 2-methyl-, acetate	624-41-9	**393,3**	**312,4**	yes
Hexanoic acid, ethyl ester	123-66-0	11010,7	10120,6	no
Acetic acid, hexyl ester	142-92-7	**170,1**	**152,8**	yes
Octanoic acid, ethyl ester	106-32-1	**12 860,3**	**14 350,5**	yes
Butanedioic acid, diethyl ester	123-25-1	137,8	116,9	no
Decanoic acid, ethyl ester	110-38-3	**1 998,8**	**4 165,7**	yes
	Total Esters	**117 452,0**	**110 308,9**	
Ethers				
	Total Ethers	**436,5**	**357,6**	
Furans				
	Total Furans	**228,2**	**191,7**	
Halogen-containing compounds				
	Total Halogen-containing compounds	**89,8**	**0,0**	
Ketones				
	Total Ketones	**593,4**	**458,5**	
Nitrogen-containing compounds				
	Total Nitrogen-containing compounds	**0,2**	**0,2**	
Oxygen-containing compounds				
Propanoic acid, 2-hydroxy-, ethyl ester	97-64-3	**12 473,6**	**11 457,3**	yes
	Total Oxygen-containing compounds	**12 516,0**	**11 581,1**	
Sulfur-containing compounds				
	Total Sulfur-containing compounds	**3,6**	**4,5**	
	Total VOC	**268 755,3**	**259 227,4**	

(*) The concentration of this compound cannot be determined accurately

The concentrations in bold and red exceed the odour threshold value (OTV)

The concentrations in bold and green don´t exceed 0.1 ug/m3

In total 71 chemical compounds have been identified by GC-TofMS. Some of them are present only in one of the bottles. Some others are present in both bottles but in different concentrations.

The main chemical families represented are alcohols, esters, oxygen-containing compounds and aldehydes. The total COV concentration is higher in the [redacted] bottle (268 755,3 µg/m^3) than in the PROCORK bottle (259 227,4 µg/m^3).

Focus on acetate and ethyl esters

Esters are known to be associated with the fruity and floral characters of the wine. Both ethyl esters and acetate esters have been identified in the samples.

Major ester compound is ethyl acetate. Ethyl acetate has a sweet and fruity smell at low concentrations but at higher concentrations it brings solvent and nail polish remover unwanted notes. The ethyl acetate concentration measured in the [redacted] sample (75 095,4 µg/m^3) is higher compared to the Procork bottle (67 436,3 µg/m^3) (+11,4%). In both bottles, the concentrations measured are 1 to 50 times greater than their theoretical OTV, meaning this compound may participate to the overall flavor of the wine.

Other acetate esters have been identified (isobutyl acetate, 3 -methylbutyl acetate (isoamyl acetate), 2-methylbutyl acetate). For all of them the concentration measured is above the theoretical OTV and higher in the [redacted] bottle than in the Procork bottle.

Ethyl esters have also been identified. Short chain ethyl esters concentrations (ethyl propanoate, ethyl butanoate, ethyl hexanoate) are higher in the [redacted] bottle than in the Procork bottle. On the reverse medium chain ethyl esters concentrations (ethyl octanoate and ethyl decanoate) are higher in the Procork bottle compared to the [redacted] one. Methyl branched ethyl esters concentrations (ethyl 2-methyl propanoate, ethyl 3-methyl butanoate) are almost similar in both bottles.

4.2 Comparison of GC-TofMS results to a professional tasting

Prior to the GC-TofMS analyses conducted here, a professional tasting of the wine was conducted in February and April 2020 by Jean-Marc Quarin, an independent Bordeaux based wine critic. His summary is shown below.

Jean-Marc Quarin
Chablis 1er cru, Fourchaume, [redacted] 2018
Comparative tasting with Procork technical cork stopper versus [redacted] stopper

Conclusion and hypotheses on the first tasting made on February 16, 2020 and continued on April 3, 2020

1) In this first series of open bottles, the [redacted] corking seems more tannic, which removes the silky mouth feel from the wine, especially between the middle and the finish where I have spotted both more acidic and more bitter notes.
2) The Procork corking induces a more regular stimulation of the wine between the entry in the mouth and the finish (no loss of silky mouth feel). The balance of sensations is better respected.
3) [redacted] is regular in the presence of freshness on the nose.
4) Procork is regular in the presence of more ripe fruit and silky mouth feel on the palate. To note that this maturity does not take away from the freshness.
5) There are 2 different styles.

Conclusion and hypotheses of the second tasting of April 3 and 6, 2020

1) [redacted] shows a difference from one bottle to another. Presence of more acidity marked the first time verses the second and a bitter shade the second time.
2) [redacted] is regular in the presence of freshness on the nose.
3) Procork is regular in the presence of more ripe fruit and silky feel on the palate.
4) In the 2 tests Procork presents a wine very well constructed on the palate. It respects the 3 best stimulation times: presence on attack, presence in the middle, presence in the finish. In addition, the aromatic part reveals regularity in the presence of ripe fruit ("exotic fruit") or sometimes creamy. It is very stable.
5) One might think that the wine corked by Procork will keep its qualities over time. After three days of opening, it picked up tension in the body while keeping the silky mouth feel mentioned at the start while the [redacted] wine loses its qualities.

A major sensory difference noticed by Mr Quarin is related to the ripe fruit character of the wine which is more present in the Procork bottle compared to the [redacted] bottle. Therefore, the interpretation of the molecular analysis here, focuses on this major difference.

The fruit character of wine is mainly derived from esters. The different ratios and combinations of the diverse esters present in wine bring about a range of fruit characters including for example blackberry, strawberry, apple, and tropical fruit notes. Due to complex synergistic effects, ester combinations create a totally different aroma compared to their individual aroma characteristics.

Compared to other fruits, grapes do not contain a significant quantity of esters. However, the wine does contain relatively high concentrations of esters which are produced by the yeast during fermentation from precursors in the grapes. These esters contribute to the range of intense fruit and floral characters of the wine. Winemakers attempt to control the fruit character by controlling the fermentation conditions and the yeasts involved because wild yeasts produce unpredictable results. In highly sought-after wines, terroir is the ultimate decider of the fruit character and the winemaker is just the custodian of the process.

The ester profile resulting from fermentation then evolves as the wine ages due to changes in the hydrolysis-esterification equilibria. Additionally, through a complex series of chemical transformations, oxidation can also affect the aroma produced by the ester profile as described in 2013 by Patrianakou and Roussis[1].

The ester, ethyl acetate, is a significant oxidation marker in wine. It is produced not only by fermentation and spoilage microbes but also by the direct oxidation of ethanol in the presence of the naturally occurring Fe3+ and Cu2+ catalysts[2]. Therefore, increased levels of the ethyl acetate, with all other factors being equal, indicates an increased level of oxidation.

The significantly higher level of ethyl acetate in the [redacted] bottle (+11,4%) compared to the same wine in the Procork bottle might therefore indicate more oxidation. Such an observation is consistent with the published high initial oxygen ingress levels of [redacted] being approximately 0,5 mg of oxygen in the first 7 days after bottling[3], and the higher overall levels of oxygen in the molecules detected in the [redacted] bottle analysed here.

Another effect of this oxidation process would be the shift in the ester profile towards the shorter chained esters observed in the [redacted] bottle. Indeed, a notable reduction of the concentration of the C8 and C10 ethyl esters, ethyl octanoate and ethyl decanoate, has been observed here in the [redacted] bottle while short chain ethyl esters (C3, C4 and C6) were present in higher concentrations. One hypothesis is that due to oxidation, the free radicals generated by the catalysts, would have non-selectively attacked and oxidized many wine constituents including their carbon chains ultimately leading to the formation of shorter chained esters. Ethyl octanoate and ethyl decanoate are significant contributors to the fruit character of the wine[1] and their observed decrease in the ester profile measured here may be the cause of the loss of ripe fruit character observed in [redacted] bottle by Mr Quarin, the professional taster.

Bibliographical reference

[1] Decrease of Wine Volatile Aroma Esters by Oxidation, M Patrianakou & I G Roussis, South African J Enol. Vitic. 2013, 34, 2
[2] Handbook of Enology Vol 2 P Ribereau-Gayon, Y Glories, A Maujean, D Dubourdieu P213
[3] Impact of stoppers on the aging of wine in bottles, V. Chevalier, A. Pons, C. Loisel, Revue Des Oenologues N° 170 January 2019

5 Conclusion

In this study, two bottles of Chablis 1er cru, Fourchaume, [redacted] 2018, have been compared: one closed with [redacted] technical cork; the other closed with a technical cork coated with the Procork membrane.

Molecular analyses have been performed by GC-TofMS on the headspace of the two wine bottles. The objective of the study was to compare the composition in volatile organic compounds of both wines and see if any correlation could be made with the tasting evaluations of the independent wine critic Jean Marc Quarin. The Procork bottle has been described by the taster as having a more ripe fruit character than the [redacted] bottle.

This study measured higher quantities of ethyl acetate in the [redacted] bottle compared to the Procork bottle. This difference indicates there may be more oxidation in the [redacted] bottle. This suggested oxidation in the [redacted] bottle could also be the cause of the observed change in the wine esters profile which could be responsible for a loss of the ripe fruit character noticed by the professional taster, Mr Quarin.