sensenet

by Odournet

Report

Client: PROCORK

Project number: ONFRPROC19C

Date : 1st August 2019

Written by: Marine Douguet

Référence : EQ-REA23
Révision : 002
Date : 05/10/2018

Your project

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

CLIENT CONTACT

Dr Gregor Christie
CEO ProCork
Tel: +61 419 599 597
Email: gregor@procorktech.com

ProCork
Suite 768 585 Little Collins Street Melbourne
VIC 3000

PROCORK

SENSENET CONTACT

Marine DOUGUET
Sensory and Molecular Analysis Consultant
SENSENET France
Tél: +33 (0)2 99 55 17 95
Mobile: + 33 (0)7 69 45 39 84
Email: mdouguet@sensenet.net

SENSENET France
By ODOURNET
3 allée de Bray
35510 CESSON SEVIGNE
www.sensenet.net
www.odournet.com

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 bitter cork lignins and taints.

A triangular test has already been conducted on synthetic wines to confirm the inertness and food neutrality of the Procork membrane by comparing a synthetic wine which has been in contact with the membrane and the “control” synthetic wine.

To further investigate the impact of the membrane on wines, Procork asked to perform molecular analyses (GC-TofMS) on the headspace of two wine bottles from the 2009 vintage: one closed with a simple cork used as a control; the other closed with a cork coated with the Procork Membrane.

This document summarises the results obtained by molecular analyses.

2 Services summary

Title: Molecular analysis on wines closed with cork coated with Procork Membrane		
Experimental Plan		
Number of samples	Two bottles of the same wine 1 closed with Procork the other as a control	
Sampling		
Protocol	Headspace extraction: the product was introduced into a micro-chamber (at 27 °C. for 10 minutes), then by helium scanning, the headspace was trapped on Tenax® tubes.	
Analyses		
Molecular analyses		
Parameters	**Methodologies**	**Details**
GC-TofMS	Internal method	Full

3 Experimental

3.1 Protocol for sample preparation

The wine used for this study was a red wine: a 2009 Fronsac (90% Merlot, 10% Cabernet Franc) from Chateau de la Dauphine.

Two different bottles were used: one labelled “N” closed with a simple cork and the second labelled “Procork” closed with a cork coated with the Procork Membrane. Those two wine bottles have been stored in the same conditions for ten years.

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.

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.

3.2 Molecular Analysis

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 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 ionised and by the Time-of-Flight (ToF) selector.

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

GC-TofMS analyses have been performed on the samples collected on the two wine bottles. The table below 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 m3 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)

sensenet by Odournet

GC-TOFMS MAIN RESULTS

Compound	CAS No.	Concentration (ug/m3)		OTV available?
		N bottle	Procork bottle	
Alcohols				
Ethanol	64-17-5	****	****	yes
1-Propanol	71-23-8	2 548,4	2 530,1	yes
1-Propanol, 2-methyl-	78-83-1	10 833,4	10 288,4	yes
1-Butanol	71-36-3	1 478,7	1 270,5	yes
1-Butanol, 3-methyl-	123-51-3	51 038,3	48 136,7	no
1-Butanol, 2-methyl-	137-32-6	31 962,1	31 277,3	yes
1-Hexanol	111-27-3	302,9	289,7	yes
Total Alcohols		98 858,5	94 448,1	
Aldehydes				
Acetaldehyde (*)	75-07-0	228,4	215,6	yes
Propanal, 2-methyl-	78-84-2	41,5	35,9	yes
Methacrolein	78-85-3	38,7	32,3	yes
Butanal, 3-methyl-	590-86-3	1 862,1	1 857,2	yes
Benzaldehyde	100-52-7	28,6	21,2	yes
Total Aldehydes		2 506,3	2 437,9	
Amines				
Total Amines		92,6	59,9	
Aromatic Alcohol				
Total Aromatic Alcohol		16,9	8,7	
Aromatic compounds				
Total Aromatic compounds		20,7	18,6	
Cyclic Hydrocarbons				
Total Cyclic Hydrocarbons		2,5	5,1	
Esters				
Ethyl Acetate	141-78-6	15 072,1	12 136,1	yes
Propanoic acid, ethyl ester	105-37-3	1 788,0	1 202,6	yes
Propanoic acid, 2-methyl-, ethyl ester	97-62-1	1 819,7	1 315,0	yes
Isobutyl acetate	110-19-0	434,4	459,4	yes
Butanoic acid, ethyl ester	105-54-4	1 807,9	1 184,8	yes
Butanoic acid, 3-methyl-, ethyl ester	108-64-5	1 546,4	1 224,3	yes
1-Butanol, 3-methyl-, acetate	123-92-2	3 154,9	2 995,1	yes
1-Butanol, 2-methyl-, acetate	624-41-9	1 040,5	973,2	yes
Pentanoic acid, ethyl ester	539-82-2	9,0	4,1	yes
Hexanoic acid, ethyl ester	123-66-0	4 118,2	3 572,6	no
Octanoic acid, ethyl ester	106-32-1	3 298,2	2 910,5	yes
Total Esters		35 951,7	29 487,0	
Ethers				
Total Ethers		237,1	223,9	
Furans				
Total Furans		110,9	132,8	
Halogen-containing compounds				
Total Halogen-containing compounds		43,1	26,3	
Heterogroups				
Total Heterogroups		13,4	11,3	
Ketones				
2,3-Butanedione	431-03-8	43,8	41,0	yes
Total Ketones		207,9	173,9	
Organic Acids				
Acetic acid	540-73-8	92,5	36,9	no
Total Nitrogen-containing compounds		92,5	36,9	
Oxygen-containing compounds				
Propanoic acid, 2-hydroxy-, ethyl ester	97-64-3	2382,7	2101,4	no
Total Oxygen-containing compounds		2 382,7	2 101,4	
Sulfur-containing compounds				
Dimethyl sulfide	75-18-3	16,6	12,7	yes
Total Sulfur-containing compounds		30,9	27,5	
Terpenes				
Total Terpenes		3,5	2,1	
TOTAL VOC		140 571,3	129 201,3	

(*) 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

****** too much quantity**

Chemical inertness of the Procork Membrane

In total 66 chemical compounds have been identified by GC-TofMS. The main chemical families represented are: alcohols, esters, aldehydes and oxygen-containing compounds.

The results of the GC-TofMS analyses performed show that no additional compounds were detected in the Procork sample compared to the control one. This confirms the absence of molecules released by the Procork membrane into the wine after ten years storage.

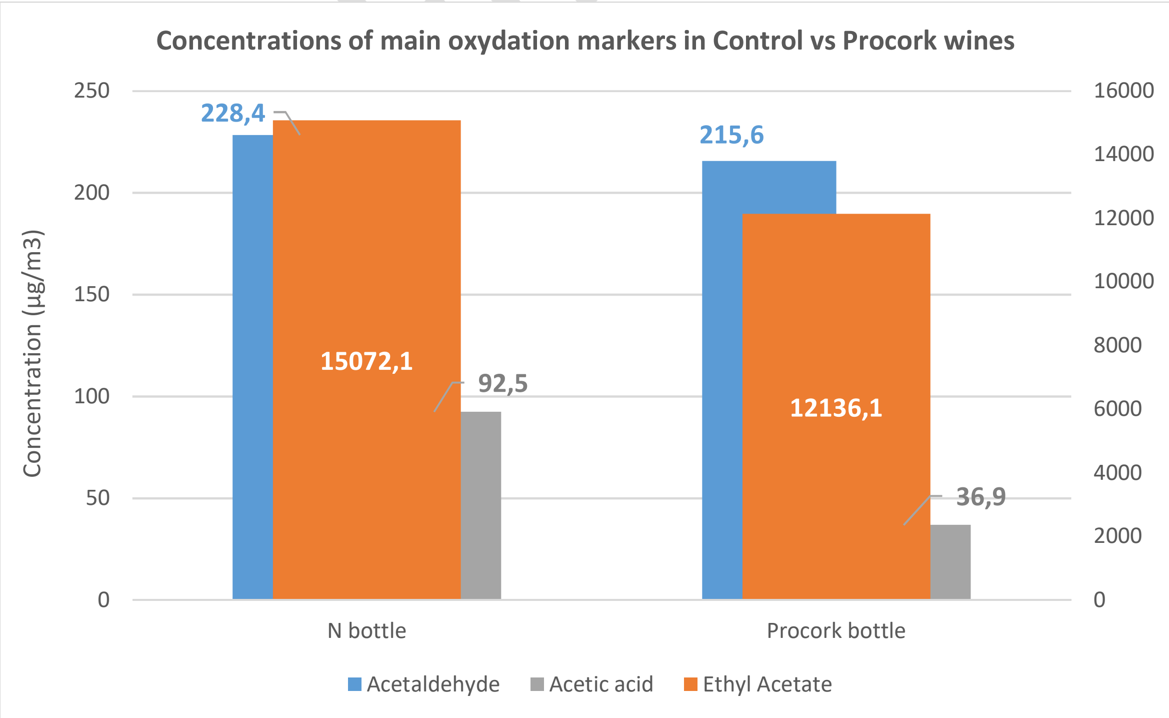
This study thus demonstrated the chemical inertness of the Procork membrane towards red wines after ten years.

Impact of Procork Membrane on wine oxidation main markers

After wine bottling, oxidation can occur in the bottle. During oxidation, ethanol can be oxidised in acetaldehyde which in turns can generate acetic acid. Those oxidised compounds can be responsible for flavors taints and faults. This chemical reaction cascade occurs because of catalysts present in the complex wine mixture. Another common marker studied is ethyl acetate which is generated by esterification from ethanol and acetic acid.

Acetaldehyde gives a sherry, pungent and metallic character to the wine, acetic acid gives sharp, vinegar, acid notes. Ethyl acetate has a sweet and fruity smell at low concentrations but at higher concentrations it brings solvent and nail polish remover unwanted notes. All those three compounds can thus negatively impact the flavour of the wine.

The graph below shows the concentrations of acetaldehyde, acetic acid and ethyl acetate measured in both samples. For the three markers, the concentrations measured in the control sample are higher compared to the Procork bottle. The percentage of increase are quite significant, especially for acetic acid (+60%) and ethyl acetate (+19%).



For those three compounds the concentrations measured are above their theoretical OTV. The concentration measured is 50 to 100 times greater than theoretical OTV in both samples for acetaldehyde and 1 to 10 times greater than OTV in both samples for acetic acid and ethyl acetate. Meaning that all those compounds may participate to the overall flavor of the wine. The higher values measured in the control wine may lead to higher expression of those undesired flavors into the wine. In particular, the Procork wine may thus appear to be less acid than the control wine.

We can assume the Procork membrane applied on the cork impacts its porosity and the oxygen supply to the wine, leading to lower concentrations of oxidation markers into the wine.

5 Conclusion

Molecular analyses have been performed by GC-TofMS on two bottles of the same 10-years old red wine (a 2009 Fronsac from Chateau de la Dauphine): a bottle closed with a cork coated with the Procork membrane and a control bottle closed with a simple cork. The objective of the study was to compare the chemical composition of both wines.

This study showed that no additional chemical compounds are released from the membrane into the wine. It thus confirmed the chemical inertness of the Procork membrane towards this red wine.

Focusing on the wine oxidation chemical markers acetaldehyde, acetic acid and ethyl acetate we showed that the Procork wine contains lower concentrations of those oxidation compounds. All those three markers are known to negatively impact the wine flavor imparting respectively metallic/pungent, vinegar/sour, solvent/nail polish remover notes.

We can assume the Procork membrane applied on the cork impacts cork porosity and oxygen supply to the wine, leading to lower concentrations of oxidation markers into the wine.

Annex 1: Detailed GC-TofMS results

		Concentration (ug/m3)		
Compound	CAS No.	N bottle	Procork bottle	OTV available?
Alcohols				
Ethanol	64-17-5	****	****	yes
Isopropyl Alcohol	67-63-0	292,5	301,1	yes
1-Propanol	71-23-8	2 548,4	2 530,1	yes
2-Buten-1-ol, 3-methyl-	556-82-1	17,4	16,0	no
1-Propanol, 2-methyl-	78-83-1	10 833,4	10 288,4	yes
1-Butanol	71-36-3	1 478,7	1 270,5	yes
1-Butanol, 3-methyl-	123-51-3	51 038,3	48 136,7	no
1-Butanol, 2-methyl-	137-32-6	31 962,1	31 277,3	yes
1-Pentanol, 4-methyl-	626-89-1	65,3	49,0	no
1-Pentanol, 3-methyl-	589-35-5	159,1	131,8	no
1-Hexanol	111-27-3	302,9	289,7	yes
Phenylethyl Alcohol	60-12-8	160,4	157,6	no
Total Alcohols		**98 858,5**	**94 448,1**	
Aldehydes				
Acetaldehyde (*)	75-07-0	228,4	215,6	yes
Propanal, 2-methyl-	78-84-2	41,5	35,9	yes
Methacrolein	78-85-3	38,7	32,3	yes
Butanal, 3-methyl-	590-86-3	1 862,1	1 857,2	yes
Butanal, 2-methyl-	96-17-3	169,5	136,6	no
2-Butenal, 2-methyl-	1115-11-3	131,1	131,8	no
2-Butenal, 3-methyl-	107-86-8	6,4	7,4	no
Benzaldehyde	100-52-7	28,6	21,2	yes
Total Aldehydes		**2 506,3**	**2 437,9**	
Amines				
Aziridine, 2-methyl-	75-55-8	74,0	38,3	no
Ethylenimine	151-56-4	18,6	21,6	no
Total Amines		**92,6**	**59,9**	
Aromatic Alcohol				
Benzyl alcohol	100-51-6	16,9	8,7	no
Total Aromatic Alcohol		**16,9**	**8,7**	
Aromatic compounds				
Benzene	71-43-2	12,2	9,4	yes
Toluene	108-88-3	3,7	1,5	yes
p,m-Xylene	108-38-3/106-42-3	2,6	5,9	yes
Styrene	100-42-5	2,2	1,7	yes
Total Aromatic compounds		**20,7**	**18,6**	
Cyclic Hydrocarbons				
Cyclopropane, ethyl-	1191-96-4	1,2	4,9	no
Cyclopropane, pentyl-	2511-91-3	1,3	0,2	no
Total Cyclic Hydrocarbons		**2,5**	**5,1**	
Esters				
Ethyl formate	109-94-4	136,3	98,7	yes
Acetic acid, methyl ester	79-20-9	259,0	190,6	yes
Ethyl Acetate	141-78-6	15 072,1	12 136,1	yes
Propanoic acid, ethyl ester	105-37-3	1 788,0	1 202,6	yes
n-Propyl acetate	109-60-4	89,0	68,5	yes
Propanoic acid, 2-methyl-, ethyl ester	97-62-1	1 819,7	1 315,0	yes
Isobutyl acetate	110-19-0	434,4	459,4	yes
Butanoic acid, ethyl ester	105-54-4	1 807,9	1 184,8	yes
Acetic acid, butyl ester	123-86-4	16,4	16,7	yes
Butanoic acid, 2-methyl-, ethyl ester	7452-79-1	1 034,3	885,1	no
Butanoic acid, 3-methyl-, ethyl ester	108-64-5	1 546,4	1 224,3	yes
1-Butanol, 3-methyl-, acetate	123-92-2	3 154,9	2 995,1	yes
1-Butanol, 2-methyl-, acetate	624-41-9	1 040,5	973,2	yes
Pentanoic acid, ethyl ester	539-82-2	9,0	4,1	yes
Hexanoic acid, methyl ester	106-70-7	15,4	8,5	no
Hexanoic acid, ethyl ester	123-66-0	4 118,2	3 572,6	no
Octanoic acid, ethyl ester	106-32-1	3 298,2	2 910,5	yes
Decanoic acid, ethyl ester	110-38-3	312,1	241,2	yes
Total Esters		**35 951,7**	**29 487,0**	
Ethers				
1,3-Dioxolane, 2,4,5-trimethyl-	3299-32-9	117,4	111,1	no
Pentane, 1-ethoxy-	17952-11-3	21,5	23,3	no
Butane, 1-(ethenyloxy)-3-methyl-	39782-38-2	10,5	9,7	no
Propane, 2-ethoxy-	625-54-7	87,8	79,8	no
Total Ethers		**237,1**	**223,9**	
Furans				
Furan, 3-methyl-	930-27-8	14,6	16,7	no

Furan, tetrahydro-3-methyl-	13423-15-9	96,4	116,1	no
Total Furans		**110,9**	**132,8**	
Halogen-containing compounds				
Butane, 1-chloro-3-methyl-	107-84-6	43,1	26,3	no
Total Halogen-containing compounds		**43,1**	**26,3**	
Heterogroups				
Benzophenone	119-61-9	13,4	11,3	no
Total Heterogroups		**13,4**	**11,3**	
Ketones				
Acetone	67-64-1	34,2	31,7	yes
2,3-Butanedione	431-03-8	**43,8**	**41,0**	yes
2-Butanone, 3-methyl-	563-80-4	18,5	13,1	yes
Acetoin	513-86-0	106,6	86,0	no
2-Heptanone	110-43-0	4,9	2,1	yes
Total Ketones		**207,9**	**173,9**	
Organic Acids				
Acetic acid	540-73-8	**92,5**	**36,9**	no
Total Nitrogen-containing compounds		**92,5**	**36,9**	
Oxygen-containing compounds				
Propanoic acid, 2-hydroxy-, ethyl ester	97-64-3	2382,7	2101,4	no
Total Oxygen-containing compounds		**2 382,7**	**2 101,4**	
Sulfur-containing compounds				
Carbonyl sulfide (*)	463-58-1	4,6	3,4	yes
Dimethyl sulfide	75-18-3	**16,6**	**12,7**	yes
Carbon disulfide (*)	75-15-0	9,7	11,4	yes
Total Sulfur-containing compounds		**30,9**	**27,5**	
Terpenes				
o-Cymene	527-84-4	3,5	2,1	no
Total Terpenes		**3,5**	**2,1**	
TOTAL VOC		**140 571,3**	**129 201,3**	

(*) 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

****** too much quantity**

Colour code:

- **<1 x theorical olfactory threshold**
- **1-10 x theorical olfactory threshold**
- **10-50 x theorical olfactory threshold**
- **50-100 x theorical olfactory threshold**
- **100-1000 x theorical olfactory threshold**
- **>1000 x theorical olfactory threshold**