The impact of the Diamant® process on the organoleptic characteristics of ground cork.

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Introduction

Cork has been used for many years as a closure for Wines & Spirits. With its exceptional and unparalleled physical properties, cork remains the ultimate solution for perfect wine preservation.

However, due to increasing consumer demands for a 'zero defect' product, the cork industry has been compelled to develop technical solutions to provide perfectly homogenous closures in respect of both their physical properties and the guaranteed absence of organoleptic deviations. Numerous research projects have focused on the eradication of the "mouldy tastes and smells" related to the presence of molecules from the chloroanisole family and in particular 2, 4, 6-trichloroanisole (TCA).
Numerous cork manufacturers are today offering innovative methods in an attempt to provide a solution to the 'cork taint' problem.

Oeneo Bouchage has thus developed, in conjunction with the Supercritical Fluids and Membranes Laboratory at Pierrelatte (Atomic Energy Council), a supercritical CO^2 extraction process (the Diamant® process) that eliminates, with the highest possible extraction efficiency, the undesirable organic target compounds; chloroanisoles and their precursors (chlorophenols).

The principle of supercritical fluid extraction is described in article "Supercritical fluids: an innovation for cork - Part 1/2" **(1)**. The different validation phases of the Diamant® process are included in the article "Supercritical fluids: an innovation for cork - Part 2/2" **(2).**

These articles confirm that at the industrial phase the results for releasable residual TCA are consistently below the quantification limit of the analytical method (<0.5ng/L) and that the organoleptic performance of the Diam® closure is excellent.
(AWRI - 36 months).

Throughout the validation phase of this process and during comparative tasting tests conducted by dozens of customers and prospective customers worldwide, it became apparent to Oeneo Bouchage that wines sealed with the Diam® closure are distinguished by their sharper organoleptic properties, superior fruitiness, and a cleaner taste (Wine Estate Special edition 2005).

Acting upon these results, in early 2005 Oeneo Bouchage initiated a research program with the objective of verifying whether the sensorial clarity of Diam® sealed wines is uniquely correlated to the eradication of 2,4,6-Trichloroanisole or the extraction of other aromatic molecules present in cork.

The work discussed in this article summarises the preliminary results of this study.

Matter and methods

Matter analysed

In order to accentuate any discrepancies both in terms of the sensory descriptors and the analytical results, we have decided to work directly with ground cork and its respective extracts (recovered at the separator outlet after CO^2 expansion).

Over a period of 2 months, 5 production batches of ground cork (before and after the Diamant® process treatment) were randomly picked in order to work on ground cork samples that were as diverse as possible. The concentrations of 2, 4, 6-releasable TCA ranged between 10 and 15 ng/l for the untreated ground cork and were below the limit of quantification for the treated cork.

As the Diamant® process is now industrialized; we had the opportunity to work with extracts obtained from the extraction of molecules by supercritical CO^2 on multiple batches of cork (6 tons in total). These extracts are highly concentrated which allowed us to gain access to molecules that are naturally occurring in cork in very small concentrations or in trace amounts. The extracts are delivered in the form of an emulsion with a slight supernatant fraction. The liquid and solid fractions were separated using membrane filtration and subsequently analysed individually.

(1) Lumia Guy and Perre Christian, Supercritical fluids - an innovation for cork - Part 1/2. Revue des Œnologues n° 117 spécial, 2005.
(2) Lumia Guy and Perre Christian, Supercritical fluids - an innovation for cork - Part 2/2. Revue des Œnologues n° 118 spécial, 2006

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Table 1: **Inventory of the identified molecules in the liquid and solid fractions of the Diamant® process extract.**

Composés	Méthode	m/z	Extrait Fraction liquide	Fraction solide
2-propanone	MS	43-58	D	
2-butenal	MS	41-69-70	D	
3-buten-2-one,3-methyl	MS	43-69-84	D	
pentanal	MS	41-44-57-58	D	
butanal,3-methyl-	MS	44-58-71-86	D	
acetic acid	MS	43-45-60	D	
furan,tetrahydro-2,5-dimethyl	MS	41-43-56-85	D	
2-propanone-1-hydroxy	MS	43-74	D	
1-pentanol	MS	42-55-70	D	
2-buten-1-ol,3-methyl ou 3-buten-2-ol,2-methyl	MS	41-53-71-86	D	
2-butenal-3-methyl	MS	41-55-84	D	D
2-hexanone ou 3-hexanone	MS	43-58	D	D
hexanal	MS, GC	44-56-57	D	D
2-butanone, 4-hydroxy	MS	43-70-88	D	D
furfural	MS	39-95-96	D	
2-furanmethanol ou 3-furanmethanol	MS	53-81-97-98	D	D
2-hexanone,3,4-dimethyl	MS	43-72	D	D
cyclohexene,1-acetyl	MS	81-43-109	D	D
cyclopentene, 1,2-dimethyl-4methylene	MS	77-91-93-108	D	D
2-heptanone	MS	43-58	D	D
heptanal	MS, GC	44-55-70	D	D
cyclopentene, 1-ethenyl-3-methylene	MS	91-106	D	
2-acetylfuran	MS	95-110	D	
2(5H)-furanone	MS	55-84	D	
phenol, dimethyl (2,5 ou 2,4 ou 3,4)	MS	107-122	D	D
2,5-hexanedione	MS	43-99	D	D
2-heptenal	MS, GC	41-55-83-70		D
benzaldehyde	MS	77-105-106	D	D
6-hepten-1-ol	MS	54-67-81	D	
cycloheptanol	MS	57-68-81-96	D	
1-heptanol	MS	43-56-70	D	D
1-octen-3-ol	MS, GC	43-57-72	D	D
5-hepten-2-one-6-methyl	MS	43-55-69-108	D	
beta-myrcene	MS	41-69-93		D
5-hetpen-2-ol, 6-methyl	MS	41-69-95-110	D	
decane	MS	43-57-71-85		D
octanal	MS, GC	41-57-84-69	D	D
benzene,1,4-dichloro	MS	111-146-148	D	
1H-pyrrole-2-carboxaldehyde	MS	66-94-95	D	
benzene,1- methyl-3-(1-methylethyl)	MS	91-119-134		D
limonene	MS, GC	68-93-107-136	D	D
1-hexanol,2-ethyl	MS,GC	41-57-70-83	D	
2,5 furandione,3,4-dimethyl	MS	54-82-126		D
benzyl alcohol	MS	77-79-107-108	D	D
benzene alkyl (ethyl,dimethyl)	MS	91-119		D
2-octenal	MS,GC	41-55-70-83		D
benzaldehyde,4-methyl ou (2-methyl)	MS	91-119-120	D	D
benzene alkyl (ethyl,dimethyl)	MS	91-119		D
p-cresol (phenol-4-methyl)	MS,GC	77-107-108	D	T
benzene alkyl (ethyl,dimethyl)	MS	91-119		D
guaïacol (phenol, 2-methoxy-)	MS,GC	81-109-124	D	T
benzene,1-methyl-4-(1-methylethyl)	MS	91-119-134	D	D
furan,3-[4-methyl-3-pentenyl]	MS	41-69-81-150		D
undecane	MS	43-57-71-85		D
linalol	MS,GC	55-71-93-121	D	
6-methyl-3,5 heptadiene-2-one	MS	43-79-81-109	D	D
nonanal	MS,GC	57-82-95-98		D
maltol	MS	55-71-126	D	
phenyl ethyl alcohol	MS	65-91-92-122	D	
hexanoïc acid	MS	41-60-73-87	D	

Analysis of ground cork
The sensorial approach

Comparative sensorial analyses were conducted on a ground cork macerate, before and after treatment:

- By two independent tasting panels
- In various matrixes (wine, 12% aqueous-ethanolic solution v/v acidified to pH 3.5),
- Under various conditions of storage time and temperature (10 days at 40°C - 15 days at room temperature).

The objectives are as follows:

1. Comparison of the sensorial profiles before and after treatment
2. Identification of the principal organoleptic descriptors
3. Measure the intensities of these descriptors on a scale of 0 (no defect) to 3 (saturation threshold).

The analytical approach

The ground cork is analysed by different complimentary sample preparation techniques (headspace-solid phase micro extraction, liquid-liquid extraction, solid phase extraction...).

The samples are analysed (qualitative approach) by gas chromatography coupled with mass spectrometry (GC-MS) (internal methodologies developed by GAEA Analytic). The compounds are identified by the comparison of their mass spectrum with the Nist and Wiley mass spectrum databases, or for certain molecules by the retention time and chemical standard mass spectrum.

Analysis of Diamant® extracts
The sensorial approach

The organoleptic impact of the extract is evaluated by enriching a white wine (Chardonnay) with liquid or solid fractions (dissolved in ethanol) at different percentages (0.05 - 0.1 - 0.2 - 0.4 - 0.8 - 1.6 and 3.2% - v/v). The sensorial analyses are conducted by two independent tasting panels. The objectives are as follows:

1. Compare the sensorial profiles of control sample white wine and the loaded white wine
2. Identification of the principal organoleptic descriptors
3. Measure the intensities of these descriptors on a scale of 0 (no defect) to 3 (saturation threshold).

Table 1 (cont.): Inventory of the identified molecules in the liquid and solid fractions of the Diamant® process extract.

Composés	Méthode	m/z	Extrait Fraction liquide	Extrait Fraction solide
benzene alkyl	MS	91-119		D
benzene alkyl	MS	91-119		D
benzyl alcohol, o-methyl	MS	91-104-107-122	D	D
benzene,1,2-dimethoxy	MS	77-95-123-138	D	
2-nonenal	MS,GC	43-55-70-83		D
phenol,alkyl	MS	107-121-150	D	
benzoïc acid	MS	51-77-105-122	D	
1-nonanol	MS	43-56-70		D
p-creosol (phenol-2-methoxy-4-methyl)	MS	95-123-138	D	
octanoïc acid	MS, GC	43-60-73-85-101	D	T
4-methyl-acetophenone	MS	91-119-134	D	
alpha terpineol	MS	59-93-121-136	D	D
octanoïc acid, ethyl ester	MS	41-57-88-101-127	D	
dodecane	MS	43-57-71-85		D
decanal	MS,GC	43-57-70-82	D	D
2,5-cyclohexadiene-1,4-dione,2,3,5-trimethyl	MS	79-107-122-150	D	
ethanol,2-phenoxy	MS	77-94-138	D	
2,6 octadien-1-ol,3,7-dimethyl	MS	41-69-154	D	D
benzothiazole	MS	69-82-108-135	D	
bicyclo [2,2,1] hept-2-ene,1,7,7-trimethyl (bornylene)	MS	93-108-121-136	D	
anisole, isopropyl,methyl (isomere)	MS	149-164	D	D
anisole,isopropyl,methyl (isomere)	MS	149-164	D	D
2-oxabicyclo[2,2,2] octan-6-ol,1,3,3-trimethyl	MS	43-71-108-126	D	
bicyclo[2,2,1]heptane-2,5-dione,1,7,7-triméthyl	MS	83-109-123-166	D	
2,6 octadienal,3,7-dimethyl	MS	41-69-84-152	D	D
1-dodecene	MS	41-55-69-83	D	
nonanoïc acid	MS	60-73-115-129	D	T
2-undecanone	MS	43-58-71		D
benzene methanol,4-(1-methylethenyl) (p-cymene-7-ol)	MS	105-119-135-150	D	
nonanoïc acid, ethyl ester	MS	88-101-141	D	
4-decenoïc acid,methyl ester	MS	55-69-74-110		D
phenol-2-methoxy-4-vinyl	MS	77-107-135-150	D	
p-benzoquinone,2,3,5,6-tetramethyl	MS	93-121-136-164	D	D
benzene,1,3,5-trichloro-2-methoxy (2,4,6-trichloroanisole)	MS, GC	195-210-212	T	D
2(3H)-furanone,dihydro-5-pentyl	MS	85-	D	D
2-undecenal	MS	41-55-70-83		D
inconnu sesquiterpene	MS	105-119		D
5-tetradecene	MS	55-69-83-97		D
2-dodecanone	MS	43-58-71		D
decanoïc acid, ethyl ester	MS	43-73-88-101	D	
tetradecane	MS	43-57-71-85		D
2-undecanone,6,10-dimethyl	MS	43-58-71-180		D
vanillin (benzaldehyde-2-hydroxy-3-methoxy)	MS	106-109-152	D	
dodecanal	MS	43-57-82	D	
caryophyllene	MS	63-69-93-105		D
1,2-dimethoxy-3,5-dichloro-benzene	MS	128-163-191-206		D
naphthalene, 2,7-dimethyl	MS	115-128-141-156	D	
5,9-undecadien-2-one-6,10-dimethyl (geranyl acetone)	MS	41-43-69	D	D
vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol)	MS	93-125-137-154	D	
1H cycloprop[e]azulene, decahydro1,1,7- trimethyl-4-methylene	MS	105-119-161-204		D
2,5-cyclohexadiene-1,4-dione,2,6-bis(1,1-diméthylethyl)-	MS	135-177-205-220	D	
azulene,1,2,3,4,4a,5,6,8a-octahydro-1,4-dimethyl-7-(1-methylethenyl)	MS	105-119-204		D
inconnu sesquiterpene	MS	105-119		D
cyclododecane	MS	41-55-69-83-97		D
cis[-]-2,4a,5,6,9a hexahydro-3,5,5,9-tetramethyl (1H)-benzocycloheptene	MS	105-119-133-204		D
inconnu sesquiterpene	MS	105-119		D
benzene alkyl	MS	91-119	D	D
acetovallinone (phenol-2-methoxy-4-acetyl)	MS	108-123-151-166	D	
longifolene	MS	105-119-161-204		D
2H-pyran-2-one,tetrahydro-6-pentyl	MS	55-77-99-114	D	

The analytical approach

The same analytical approach as described previously is applied to the liquid and solid fractions of the extracts in order to verify whether or not the Diamant® process can extract aromatic molecules other than 2,4,6-TCA.

Results and discussion

Ground cork

The results of the first tasting panel (4 oenologists) in a white wine reveal different aromatic profiles between the ground cork macerates before and after treatment. Before treatment, the cork macerate presents a strong aromatic intensity characterised by the presence of predominantly corky and musty notes.

After the Diamant® process, the cork macerate is characterised by a significantly lower aromatic intensity and a remarkable clean taste associated with the absence of the corky and musty notes, and the 'in-mouth' sensations' are substantially more 'full-bodied and smooth'.

A second tasting panel (8 trained tasters) demonstrated a complete change in the aromatic profile of the ground cork treated with Diamant® in a simulated wine:

- Increased organoleptic neutrality of the treated ground cork,
- Elimination of the musty descriptor and a clear reduction in the humus/mushroom - leather/synthetic - phenol and alcohol/aggressive type notes
- Superior expression of flora and vanilla notes - **(figure 1)**.

The results of these two independent tasting panels are similar. They both confirm improved organoleptic neutrality in the treated ground cork.

They demonstrate that the elimination of certain negative notes, such as mould, mushroom, humus...results in the improved expression of other positive aromatic notes naturally occurring in cork.

Table 1 (cont. /last page): Inventory of the identified molecules in the liquid and solid fractions of the Diamant® process extract.

Composés	Méthode	m/z	Extrait Fraction liquide	Extrait Fraction solide
naphtalene,1,2,4a,5,6,8a,hexahydro-4,7-dimethyl-1-1(methylethyl)	MS	105-119-161-204		D
benzene,1-methyl-4-(1,2,2-trimethylcyclopentyl) (cuparene)	MS	105-119-132-202		D
naphtalene,1,2,3,4,4a,5,6,8a,octahydro-7-methyl-4-methylene-1-(methylethyl) (mururolene)	MS	105-119-161-204		D
3,5,9-undecatrien-2-one-6,10-dimethyl	MS	41-69-81-109-124	D	
1H-2-benzopyran-1-one,3,4-dihydro-8-hydroxy-3-methyl	MS	134-149-160-178	D	
1,6,10-dodecatrien-3-ol,3,7,11-trimethyl	MS	41-69-93-107		D
vanillic acid	MS	97-125-153-168	D	
inconnu sesquiterpene	MS	105-119		D
dodecanoic acid	MS	60-73-129-200	D	
2,6,10-dodecatrien-3-ol,3,7,11-trimethyl	MS	41-69-93-107		D
hexadecane	MS	43-57-71-85		D
inconnu sesquiterpene	MS	105-119		D
naphthalene,2,3,4,4a,5,6-hexahydro-1,4a-dimethyl-7(1-methylethyl)	MS	105-119-161-204	D	
inconnu sesquiterpene	MS	105-119		D
inconnu sesquiterpene	MS	105-119		D
inconnu sesquiterpene	MS	105-119		D
copaene ou cucubene	MS	105-119-161-204		D
inconnu sesquiterpene	MS	105-119		D
syringaldehyde (benzaldehyde, 4-hydroxy-3,5-dimethoxy)	MS	139-167-181-182	D	
inconnu sesquiterpene	MS	105-119		D
naphtalene,1,6,dimethyl-4-(1-methylethyl)	MS	153-168-183-198		D
heptadecane	MS	43-57-71-85		D
4-hydroxy-2-methoxycinnamaldehyde	MS	135-147-161-178	D	
2,6,10-dodecatrienal,3,7,11-trimethyl	MS	41-69-84		D
3,5-di-tert-butyl-4-hydroxybenzaldehyde	MS	191-203-219-234	D	
tetradecanoic acid	MS	43-55-60-73	D	
octadecane	MS	43-57-71-85		D
benzophenone,2,4,6-trimethyl	MS	77-147-209-223	D	
phenol,2,3,5,6-tetrachloro-4-methoxy	MS	246-247-260-262	D	
longifolenaldehyde	MS	109-135-205-220	D	
2-pentadecanone,6,10,14-trimethyl	MS	43-58-71-109		D
1-hexadecene	MS	55-69-83-97-111	D	
nonadecane	MS	43-57-71-85		D
inconnu sesquiterpene	MS	105-119		D
hexadecanoïc acid	MS	43-60-73-129	D	
hexadecanoïc acid, ethyl ester	MS	43-88-101-157	D	
heptadecanoïc acid	MS	60-73-129-270		D
1-heptadecene	MS	55-69-83-97-111		D
9,12-octadecadienoïc,acid	MS	55-67-81-95-110		D
9-octadecenoïc acid	MS	41-55-69-83-97		D
octadecanoïc acid	MS	43-57-60-73	D	
15-heptadecenal	MS	55-69-83-97		D
1-octadecene	MS	55-69-83-97-111		D
2-nonadecanone	MS	43-58-71-85-96		D
octadecanal	MS	57-69-82-96-109		D
eicosanoïc acid	MS	57-73-129-312		D
5-nonadecene	MS	69-83-97-111-266		D
1,19-eicosadiene	MS	55-69-82-96		D
1-eicosanol	MS	57-69-83-97-111		D
3-eicosene	MS	57-69-83-97-111		D
docosanoïc acid	MS	57-73-129-140		D
1-docosene	MS	55-97-111-308		D
1-docosanol	MS	55-97-111-308		D
1-tricosene	MS	57-83-97-111-322		D
1-tetracosanol	MS	55-97-111-336		D
squalene	MS	81-121-137-149		D

MS: identification based on Nist, Wiley databases. D: detected / T: traces.
GC: identification confirmed by the retention time and chemical standard mass spectrum database.

The presence of vanilla and cocoa/toasted notes in Diamant® treated ground cork is not related to thermal degradation. The supercritical CO^2 treatment is carried out at a very low temperature (around 50°C) and is commonly used in agribusiness and perfumery with the specific aim of to preserving temperature sensitive volatile molecules.

Diamant® Extracts

The results of two independent tasting panels show a very significant change in the organoleptic profile of the wines enriched in extracts compared to the control wine sample.

For wines loaded with the liquid fraction extract, the leather/synthetic - phenol - dusty/dryness type notes occur even at the lowest concentrations with an intensity that increases with enrichment percentages. However, at the highest enrichment level, phenol, dusty and dryness descriptors are overwhelmed by the dominant cork note with a very high intensity of 10/10. An aggressive perception is perceived on the palate **(figure 2a).**

For wines loaded with a solid fraction, dusty/dryness types notes progressively evolve towards humus, woody, mushroom notes passing through a medium to strong intensity musty descriptor when the enrichment percentage increases.

At high loads, the humus, woody, mushroom descriptor is predominant with a very high intensity (10/10) **(figure 2b).**

The aromatic notes described during this enrichment study (synthetic/leather - dusty/dryness - cork - mouldy - humus/mushroom) are identical to those cited by tasting panels during organoleptic analyses carried out with untreated ground cork macerates.

Figure 1: Comparative sensorial analysis on ground cork macerates before and after the Diamant® process. Encircled descriptors indicate a significant difference (95%) when applying the chi-square test.

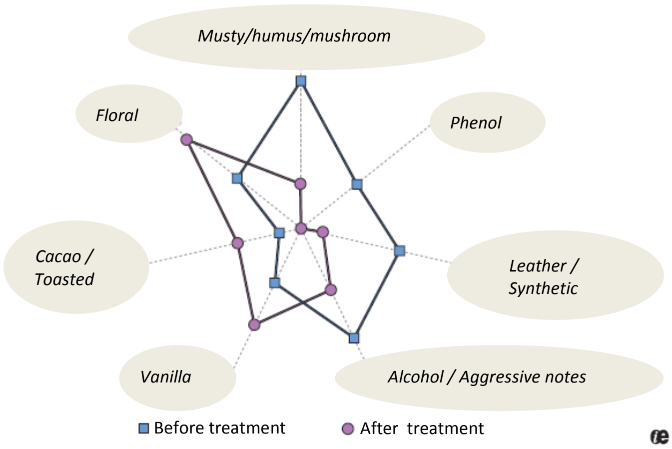


Figure 2: Results of quantitative descriptive sensorial analysis (on a scale of 10) of wine loaded with different strengths of liquid fractions (2a) and solid fractions (2b) of the Diamant® process extract.

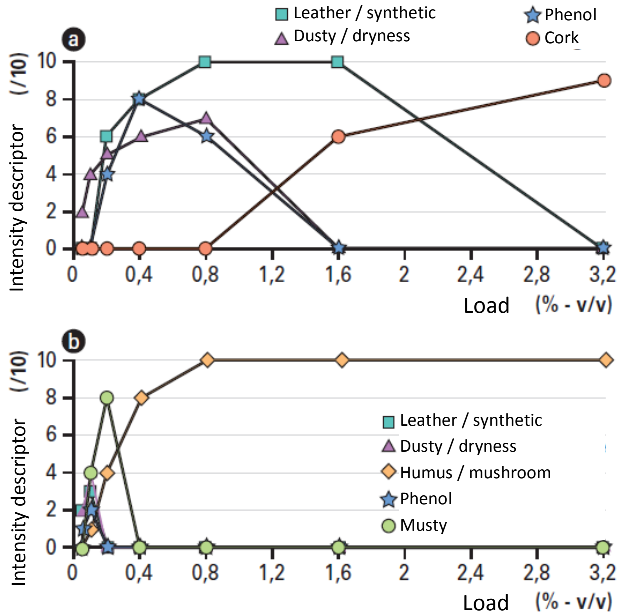


Figure 3: Chromatogram examples (total ion current mass spectrometry) of liquid fractions (3a) and solid fractions (3b) of the Diamant® process extract (preparation technique: headspace - solid phase micro extraction).

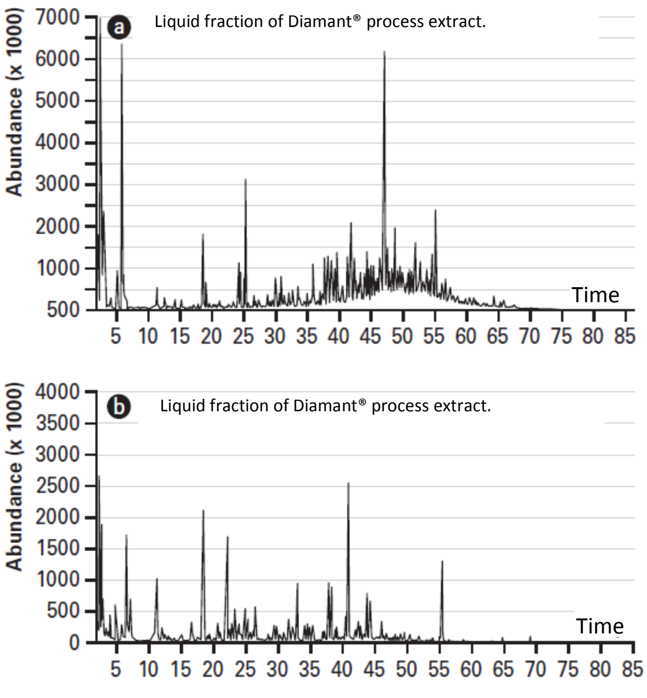
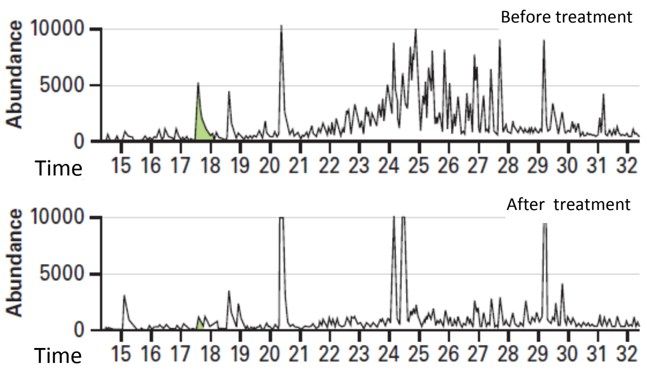


Figure 4: Examples of chromatograms of 1-octen-3-ol (mass spectrometry 57 ion extract) Ground cork before and after treatment by the Diamant® process.



The chromatographic analyses performed on the Diamant® solid and liquid fractions extracts demonstrate the presence of more than 150 molecules, a large number of which can be identified **(figures 3a, 3b and table 1).**

These molecules belong to different chemical families: alcohols, ketones, aldehydes, acids, esters, phenolics, anisoles, furans, furanones, pyranones; alkylbenzenes, hydrocarbons; terpenes, sesquiterpenes...

The chromatographic analyses performed on the cork before and after treatment show differences in the profiles of the chemical families mentioned above. For example, the impact of the process on the sesquiterpenes, the isopropyl methylanisoles (isomers), and 1-octen-3-ol is shown in **figures 4, 5 and 6**.

Certain molecules previously identified by GC-MS may be associated with the aromatic notes highlighted in this study:

- 1-octen-3-ol associated with the humus/mushroom descriptor
- p-cresol; guaiacol and octanoic acid associated with phenol - leather - synthetic descriptors.
- vanillin (and other derivatives) associated with vanilla descriptors
- furans associated with Cocoa/Toasted descriptors

These correlations were confirmed by GC-olfactometry analysis (not detailed in this article).

This study clearly demonstrates that the Diamant® process, developed for the eradication of 2, 4, 6-TCA in cork, also extract a very large number of other aromatic molecules belonging to different chemical families (alcohols, ketones, aldehydes ...).

This extraction results in a very significant change in the sensorial profile of the treated ground cork. Ground cork thus treated by supercritical CO^2 is characterized by a significantly higher organoleptic neutrality as well as by the expression of certain positive aromatic notes such as floral, vanilla or cocoa (toasted) naturally occurring in cork but under normal circumstances masked by other less positive aromatic notes such as humus/mushroom phenol - leather/synthetic ...).

These results provide an initial explanation to the remarks made by the tasting panels during the comparative tests, in particular concerning the fruitier, clean tasting characteristics of Diam® sealed wines.

This study continues today in order to quantify the molecules present in cork and to evaluate the actual degree of their organoleptic impact.

Figure 5: Examples of chromatograms of sesquiterpenes structures (mass spectrometry 119 ion extract) of ground cork before and after treatment by the Diamant® process.

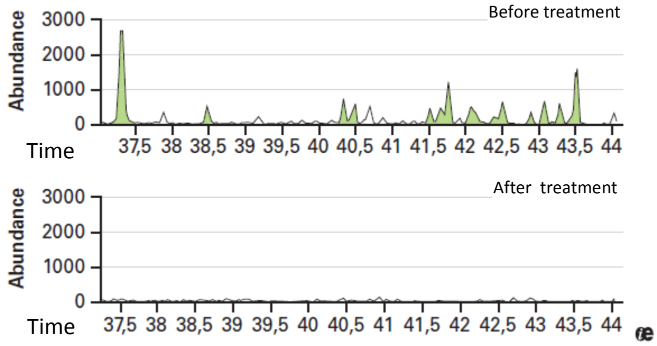


Figure 6: Examples of chromatograms of isomers of anisole isopropyl (mass spectrometry 149 ion extract) of ground cork before and after treatment by the Diamant® process.