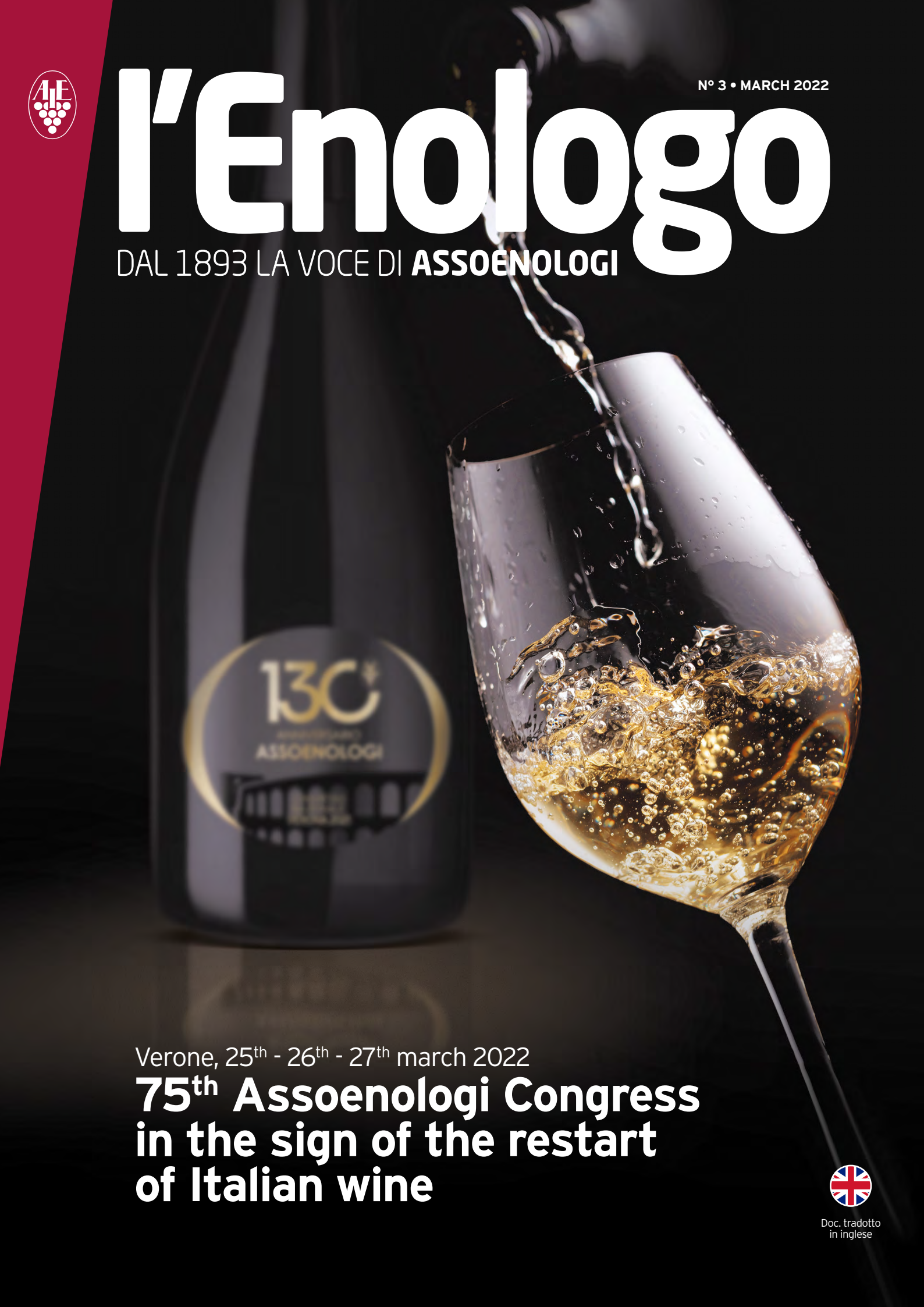
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DAL 1893 LA VOCE DI **ASSOENOLOGI**



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Doc. tradotto in inglese

MANAGEMENT OF DISSOLVED GASES DURING WINEMAKING
AND THEIR EFFECT ON WINE QUALITY

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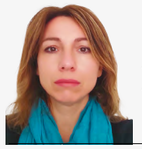
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The experiment described here assessed the impact on the aromatic composition of wine of the membrane contactor technology used to control dissolved gases.

In oenology, in cellar procedures, the management and control of dissolved gases is an important routine. Oxygen analysis is monitored at every stage: winemaking, clarification for pre-bottling and for finished product because oxygen has a decisive influence on the aroma and the flavour profile, also on the shelf life of the product. Knowing the concentration of dissolved oxygen in the wine, it is also possible to control with extreme precision the quantity of sulphur dioxide to be used during vinification, because 1 mg of O_2 reacts with approximately 4 mg of SO_2. This allows a rational response to consumer demands to reduce the quantity of sulphur dioxide added to wines, as an antioxidant.

CO_2 control and analysis play an important role during maturation (which requires the involvement of oxygen) and during pre-bottling by monitoring the sensory effect on the wines. They are also essential for checking the legal limits in still, sparkling, and semi-sparkling wines.

Oxygen management

In the case of white and rosé wines, during maturation and bottling, poor oxygen management significantly alters their aromatic profile and leads to a premature loss of fruit aromas; in particular those characteristic of polyfunctional thiols, present in some wines, which are very sensitive to oxidation and responsible for grapefruit, blackcurrant and passionfruit notes.

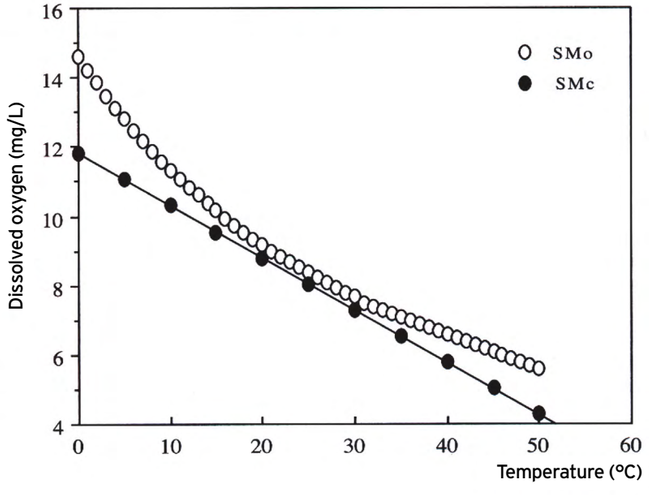
The operations of racking, clarification, blending, filtration, and bottling involve a significant dissolution of oxygen, which will be even more important the colder the wine, due to the greater solubility of this gas in the wine at low temperature (**graph 1**). Table 1 shows the values extracted from the scientific literature indicating the dissolution of oxygen in must and wine in contact with air, during different oenological processes.

It should be noted that a wine at 20°C (68°F) and atmospheric pressure cannot contain more than 8.4 mg/L of oxygen, which is said at these conditions to be

Oenological processes	O_2 dissolved mg/L
Racking	**1 - 2**
Racking in contact with air	**4 - 8**
Barrel topping up	**0,1 - 1**
Filtration with kieselguhr	**0,5 - 2,5**
Cold tartaric stabilisation	**3 - 6**
Centrifugation	**1 - 2,5**
Bottling	**0,2 - 4**

Tab. 1 - Dissolution of oxygen in must and wine in contact with air, during the main oenological processes

saturated. This value obviously varies according to temperature and pressure. Oxygen is usually solubilised at the beginning and end of the racking processes when the pipes connected to the pump are empty. It is wise to use inert gases them before starting all cellar operations, since when the pump is working properly during racking, oxygen dissolution is low. Great attention should also be paid on inerting the tanks, not to make useless all preventive operations against oxidation. The size of the container is also important, because oxygen may have a greater negative effect if the handled volumes of wine are limited. When racking barrels considerable amounts of gas may become dissolved. If necessary, deoxygenation by *stripping* can be carried out by dispersing an inert gas into the wine to reduce the concentration of dissolved oxygen. For greater efficiency, this operation should be carried out with very pure nitrogen. Regarding the choice of the *stripping* gas, bottled nitrogen is recommended instead of nitrogen produced with a nitrogen generator, and preferred purity is 99.9% rather than 99.5%. This technique should be used with great care because it can organoleptically affect the wine by causing the removal of many lightweight aromatic compounds. For higher quality results, it is preferable to carry out *stripping* in-line (pipes) rather than statically, i.e., in tanks. However, the efficiency of the "static" practice can be improved by halving the amount of nitrogen used and repeating the operation a second time, paying attention to the temperature of the wine.



Graph 1 - Dissolved oxygen saturation threshold curve according to temperature SMo: theoretical curve SMc: curve measured experimentally in water with electrode C

Carbon dioxide management

Modern wine consumers are looking for smooth and elegant products, without excessive CO_2 concentration because of its negative connotation. In the tasting equilibrium of the wine, CO_2 contributes to increase the perception of acidity and to enhance the bitterness and the astringency associated with tannins. Therefore, if the wine is acidic and tannic the level of carbon dioxide in the wine should be lower. It is essential at bottling to adjust the dose according to the commercial objective, paying more attention to the grapes variety which give typically tannic wines. When tasting, the colder the wine is served the less carbon dioxide is perceived: the threshold of perception at 20°C (68°F) is about 500 - 600 mg/L. When the wine is uncorked there shouldn't be any fizziness.

In the literature, the recommended values for CO_2 concentration during bottling are

• light, slightly tannic red wines:
500 - 700 mg/litre
• red wines for maturation:
300 - 400 mg/litre
• white and rosé wines:
600 - 1000 mg/litre
• sweet white wines and rosé:
400 - 600 mg/litre.

It is also worth considering that the CO_2 contained in the wine acts as a partial protection against oxidation: indeed, on contact with air (oxygen), the dissolved CO_2 is released, thus slowing down the rate of oxygen dissolution.

In decarbonization, by injecting micro-bubbles of nitrogen, the oxygen molecules are the first to be eliminated because they are the most volatile. CO_2, being much more soluble in wine, is even more difficult to eliminate. Temperature is a fundamental parameter. This operation is ineffective below 12°C (53,6°F). A wine at 14°-15°C (57,2°-59°F), or even 18°C (64,4°F), will ease decarbonization. If properly managed, this operation may reduce the CO_2 content by about 500 mg/l. The gas flow rate used for decarbonization should be higher than for deoxygenation.

Use of molecular sieve membrane contactor technology

New methods of managing gases have been developed in cellars in recent years. These include the use of membrane technologies acting as molecular sieves and allowing low weight molecular gas exchange to be managed with great accuracy and repeatability.

The precise management of gases dissolved in wine, primarily oxygen and carbon dioxide, but also the elimination of hydrogen sulphide and acetaldehyde, thanks to these systems, is an important innovation and a useful tool for oenological applications in the cellar. Indeed, the regulation of gases in wine allows a considerable improvement in the sensory quality of the finished products. It also means a significant reduction in the use of sulphur dioxide and ascorbic acid, and an extended shelf life while maintaining the aromatic, chromatic and taste characteristics of the wines for a longer time.

Materials and methods

The experimental trial

In July 2020, at the Ferraia estate in Ziano Piacentino (Italy), tests of oxygen elimination and carbon dioxide regulation were carried out on three wines: *two white wines, Sauvignon Blanc and Ortrugo* (the latter is an autochthonous grape variety that is slightly aromatic and generally rich in terpenes from the hills of Piacenza) *and a red wine, Gutturnio*, a blend of Barbera and Croatina grapes.

Vinext's EquilibriO2 system was used for the tests. (**Figure 1**) EquilibriO2 uses a hydrophobic membrane also known as a membrane contactor. It is a hollow fibre membrane where the gas flows inside the fibres (called lumen side) while the wine flows outside the fibres in the opposite direction (called shell side). Due to the difference in concentration and partial pressure of the gases, a gas exchange takes place. Thus, the gas concentration is regulated without direct contact between the technical gas and the wine, unlike techniques based on stripping. The prevalence of gas exchange between the different gas molecules dissolved in the wine is due to the difference in molecular weight of the different gases.

The light weight dissolved gases, as nitrogen, oxygen, and hydrogen sulphide, leave the wine quickly, while the higher weight molecular carbon dioxide needs more tension to pass through the pores of the fibres. Thus the treatment reduces the dissolved oxygen, nitrogen and hydrogen sulphide by more than 90%, while carbon dioxide can be reduced, maintained or, if necessary, increased.

The system measures the concentration of O_2 and CO_2 automatically and in real time thanks to precision sensors. These controllers guarantee accuracy and full automation of the operation. The best results, both in performance and accuracy of gas management, were obtained with the generation of a slight vacuum in the gas side of the membrane (lumen side).

Samples of each wine were taken before and after the passage through the system to evaluate the influence of the gas removal and regulation treatment on the wine. A complete screening of the aromatic compounds of the treated wines was performed, to monitor the sensory effect on the obtained products. In addition, water from the plant's vacuum pump water loop was also sampled.

The aim was to exclude the risk of depletion of the aroma component as a result of the treatment. Analysis of the loop water where the gases escaped allowed us to verify the possible presence of aroma compounds "stripped" from the wine.

Figure 1 - EquilibriO2 20.120 model



Analysis of aromatic compounds

The two samples of each wine (Sauvignon Blanc, Ortrugo and Gutturnio), taken before and after the treatment, and the three respective water samples taken during the process, were analysed by GC-MS for the determination of volatile compounds to assess the impact of the treatment on the overall aroma of the wine. The volatile component of each sample was isolated by solid phase extraction (SPE, C18 EC cartridges) and analysed using standard gas chromatography-mass spectrometry (GC-MS) techniques to evaluate the aromatic compounds related either to the fermentation or to the varietal origin of the wines. Both compounds were quantified: those present in the "lipophilic" fraction, the one retained by the cartridges, are richer in aromas, and those of the "hydrophilic" fraction -- not retained -- are rich mainly in more polar compounds typical of yeast metabolism.

The GC-MS used for the aroma analysis is an Agilent 7890 equipped with an Agilent 5975 single quadrupole Mass Selective Detector (MSD).

The compounds were separated on a 60 m HP-Innovax fused silica capillary column, 0.25 mm internal diameter, 0.25 µm film. The carrier gas was helium with a purity of 99.9999% and a constant flow rate of 1 ml/minute. Sample injection was performed in splitless mode at 40°C (104°F) with a *purge* time of 2 minutes. The injector temperature was maintained at 250°C (482°F) and the interface temperature at 230°C (446°F). The oven temperature gradient followed

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this pattern: 40-60°C (104-140°F) at 3°C (37,4°F)/min, isotherm at 60°C (140°F) for 2 min, 60°C-190°C (140-374°F) at 2°C(35,6°F)/min and 190°C-230°C (374-446°F) at 5°C (41°F)/min with final isotherm of 15 min. The molecules were identified by comparing the linear retention index (LRI) and MS spectra with the same parameters reported in the literature or stored in the library of the identification program (Chemstation, Agilent) or, when possible, with those measured by injecting pure reference compounds into the gas chromatograph.

Results

Wine treatment in the cellar

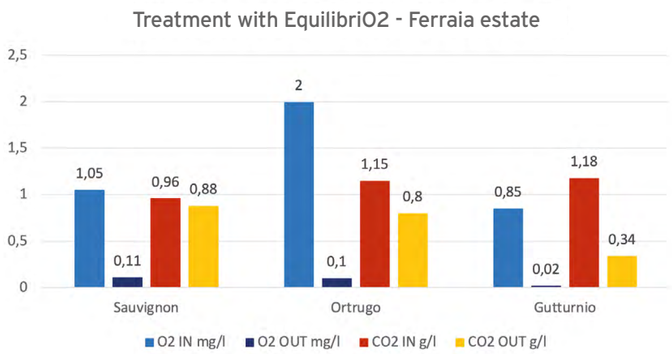
The EquilibriO2 system was used during the racking of the wines. The test was performed on 3 different wines:

1. Sauvignon Blanc: removal of O_2 and preservation of the CO_2
2. Ortrugo: maximum oxygen reduction and partial CO_2 reduction
3. Gutturnio: maximum gas extraction mode with total O_2 reduction (about 95%) and CO_2 reduction of about 70%.

Graph 2 shows the results of the 3 tests:

The aromatic profile of the wines

Table 2 shows the concentrations of the main volatile compounds determined in the wines. Although the wines show significant differences in their composition, the two tests "IN" (sample before membrane treatment) and "OUT" (sample after membrane treatment) do not show particularly significant differences.



Graph 2: Oxygen and CO2 contents in experimental wines before (IN) and after (OUT) treatment.

The white wines show, as expected, a profile more characterised by the presence of esters with fruit aromas. These include *isoamyl acetate* with its characteristic banana aroma, *hexyl acetate* with pear notes, *ethyl hexanoate* with pineapple aroma, and *ethyl octanoate*, floral and tropical fruit. We also noted the very interesting presence in Ortrugo wines of terpene varietal compounds such as *linalool* (present in a concentration just above the perception threshold) which brought floral notes of orange blossom and bergamot to the wine, and *norisoprenoids* such as β-damascenone, an important odorant compound characterized by fruit aromas, quince, and peach.

The wines were also subjected to a sensory analysis (data not shown): tasters were asked to point out any differences between the samples and to identify them. The tasters clearly differentiated the wines on the reduction notes. The OUT wines were more scented, with cleaner and more intense fruit notes, which led the tasting group to prefer these wines. For the *Ortrugo*, white fruit and floral notes were more intense and cleaner in the OUT sample compared with the IN sample.

According to the tasters the *Gutturnio* gained a smoother and more elegant mouthfeel, and the perception of tannin and bitter aftertaste seemed to decrease. The Gutturnio also gained a wider aromatic expression of red fruit notes. For both samples the panel clearly preferred the treated sample rather than the original wine.

In the case of the Sauvignon IN, the boxwood and passionfruit notes were more deeply expressed than in the OUT sample, which was described as fruitier (peach and pear).

In the specific case of *Sauvignon Blanc* the use of the membrane appeared to neither improve nor interfere with the quality of the product. The panel, while recognising clear differences, did not express a preference, with half choosing the more typical IN product and half preferring the OUT sample, with had a richer but less varietal bouquet.

A very small number of compounds were detected in these samples. Small amounts of isobutyl alcohol were found only in the Gutturnio, but this concentration was also higher in the OUT wine. The presence of diethyl sulphide, with its characteristic reduced odour, was found in all the samples of the water from the plant's vacuum pump water loop. This could explain the identification of differences between the IN and OUT samples by the panel, although not always with a clear preference.

Figure 2 - EquilibriO2 20.120 model



	Sauvignon		Ortrugo		Gutturnio	
	in	out	in	out	in	out
Ethylbutanoate	95	117	90	87	55	20
Isobutyl alcohol (mg/L)	7	8	6	8	25	21
Isoamyl acetate	1005	989	2286	2399	702	642
Isoamyl alcohol (mg/L)	64	66	65	52	97	62
Ethylhexanoate	659	583	674	644	203	149
3-methyl-1-pentanol	39	41	38	25	38	39
Ethyllactate (mg/l)	6	6	15	15	42	33
Hexylacetate	257	294	174	184	17	17
Hexanol	1041	886	783	794	668	670
Trans-3-hexenol	30	26	15	20	nd	nd
3-ethoxypropanol	283	291	198	325	299	362
Cis-3-hexenol	288	250	84	79	108	115
Ethyloctanoate	1259	1175	742	886	269	274
Ethyl-2-hydroxycaproate	71	65	45	48	134	123
Benzaldehyde	25	22	19	17	10	15
Ethyl-3-hydroxybutyrate	269	239	258	294	225	289
Isobutyric acid	316	294	226	387	629	846
Hotrienol	12	19	nd	nd	nd	nd
Butyric acid	271	258	371	626	187	256
γ-butyrolactone	2968	2587	1256	1517	4971	5491
Isovaleric acid	891	774	612	804	998	1245
Ethyl decanoate	502	507	247	326	79	67
Linalool	27	23	63	65	29	26
α-terpineol	n/a	n/a	78	95	n/a	n/a
Methionol	1284	1334	744	1012	1593	1850
Diethylsuccinate	1960	1767	1427	1333	1959	2468
Ethyl-4-hydroxybutyrate	3187	2687	1053	993	4568	5844
β-damascenone (ng/l)	n/a	n/a	729	728	n/a	n/a
Benzyl alcohol	38	36	11	11	13	13
Acetovanillone	38	5	4	5	nd	nd
Diethyl glutarate	2	2	2	2	1	1
Hexanoic acid (mg/l)	20	22	42	40	24	15
Trans-2-hexenoic acid	188	189	338	394	148	121
2-phenylethyl acetate	46	41	40	33	56	47
2-phenylethanol (mg/l)	3491	2978	3833	3841	1199	1268
Octanoic acid	n/a	n/a	n/a	n/a	34	43
3,7-dimethyl-1-octene-3,7-diol	326	269	142	176	157	167
4-vinylguaiacol	n/a	n/a	n/a	n/a	n/a	2
Monoethyl-2-hydroxyglutarate	928	716	682	654	1368	1981
Diethyl-2-hydroxyglutarate	n/a	n/a	n/a	n/a	283	574
Phenylacetic acid	2009	1688	2219	2148	550	524
Decanoic acid	n/a	n/a	1625	1790	n/a	n/a
3-hydroxy-β-damascone (ng/l)	1009	1157	157	149	157	80
4-vinylphenol	n/a	n/a	n/a	n/a	6	n/a
Benzoic acid	4	n/a	n/a	n/a	n/a	n/a
Lauric acid	56	49	3	5	5	5
Vanillin	n/a	n/a	n/a	n/a	n/a	n/a
3-hydroxy-7,8-dihydro-β-ionone	104	82	666	524	659	699
Palmitic acid	n/a	n/a	49	49	n/a	n/a

Tab. 2 - Aromatic composition of Sauvignon Blanc, Ortrugo and Gutturnio wines before (IN) and after (OUT) membrane treatment. All data are expressed as μg/L equivalent of the internal standard 1-heptanol, unless otherwise stated.

Compounds	Sauvignon	Ortrugo	Gutturnio
Isobutyl alcohol	nd	nd	446
Isoamyl acetate	nd	nd	50
Isoamyl alcohol (mg/l)	n.d	1	3
Diethyl sulphide	230	280	176
Ethyl lactate	nd	114	129
4-OH-4-methyl -2-pentanone	56	41	32
Acetic acid	14	nd	nd
Benzaldehyde	5	3	5
Linalool	6	5	7
2-phenylethanol	30	100	144
Acetophenone	103	64	107
Stearic acid	21	66	nd
Palmitic acid	nd	133	nd
Guaiacol	nd	14	26

Tab. 3 - Aromatic composition of water samples taken after treatment. All data are expressed as μg/L equivalents of internal standard 1-heptanol, unless otherwise stated.

Conclusions

This experiment was done to attempt to evaluate the effect of membrane contactor technology, used to control dissolved gases, on the aromatic composition of wines, and it revealed some important results.

First, the aromatic composition of the wines before and after treatment was substantially preserved, that is it did not undergo significant modifications.

Some light molecules, especially malodorous disulphides, are eliminated by the treatment, as shown by the analysis of the water collected after the treatment.

Some interesting indications, needing further investigation, are highlighted by the sensory analysis of the wines, which showed that the OUT wines were more scented and had generally fruitier and more intense flavours than the wines tasted before treatment.

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