Oxidation Management of White Wines

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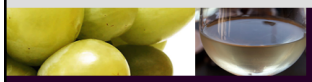
Objectives

- **Oxygen/Antioxidant :**
  - Mechanisms of consumption
- **“Resistance to Oxidation” :**
  - Shelf-Life Control
- **Random & Sporadic Oxidation :**
  - Cork Stopper



Phenylacetaldehyde

Methional

Sotolon

White Wine

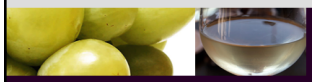
Sotolon

Porto, Sherry
Madeira Wines

A C. Silva Ferreira, T. Hogg and P. Guedes de Pinho.
J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

A C. Silva Ferreira, Barbe J.C and Bertrand A.B.
J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

Background : Key Odorants



Phenylacetaldehyde

Methional

Sotolon

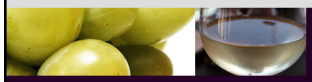
White Wine

off - Flavor

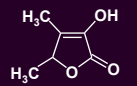
Sotolon

Porto, Sherry
Madeira Wines

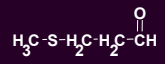
in - Flavor



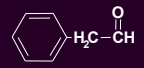
Major flavor impact compounds …



Sotolon



Methional



Phenylacetaldehyde

Rate of Formation Highly Dependent

Oxygen Regimens !!!

A C. Silva Ferreira, T. Hogg and P. Guedes de Pinho. J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

A C. Silva Ferreira, Barbe J.C and Bertrand A.B. J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

Background: Oxygen Chemistry …

O_2 *Ground State* $+e^-$

O_2^- *Superoxide Anion* (pKa = 4.5-4.9) $+e^-$ $+H^+$

$HO_2^\bullet$ *Perhydroxyl Radical* (pKa = 16-18) $+H^+$

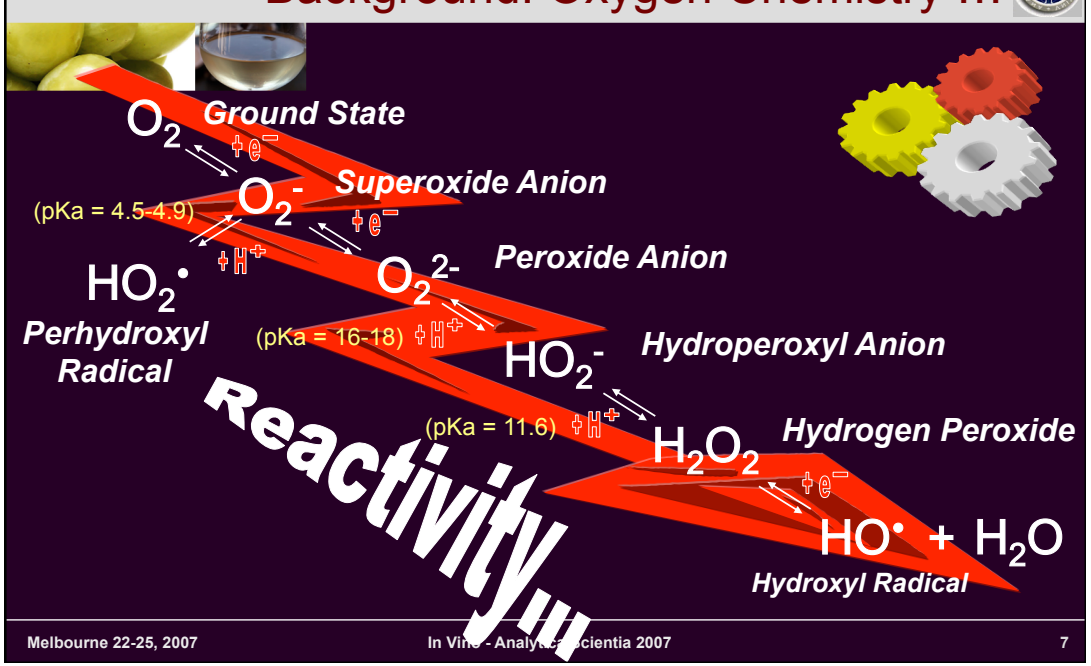
O_2^{2-} *Peroxide Anion* $+H^+$

HO_2^- *Hydroperoxyl Anion* (pKa = 11.6) $+H^+$

H_2O_2 *Hydrogen Peroxide* $+e^-$

$HO^\bullet + H_2O$ *Hydroxyl Radical*

Several Reactive Oxygen Species


Ground State
O_2
+e⁻
$O_2^{\bullet-}$
Superoxide Anion
(pKa = 4.5-4.9)
+e⁻
+H⁺
$HO_2^{\bullet}$
Perhydroxyl Radical
O_2^{2-}
Peroxide Anion
(pKa = 16-18) +H⁺
HO_2^-
Hydroperoxyl Anion
(pKa = 11.6) +H⁺
H_2O_2
Hydrogen Peroxide
+e⁻
$HO^{\bullet}$ + H_2O
Hydroxyl Radical
Reactivity...
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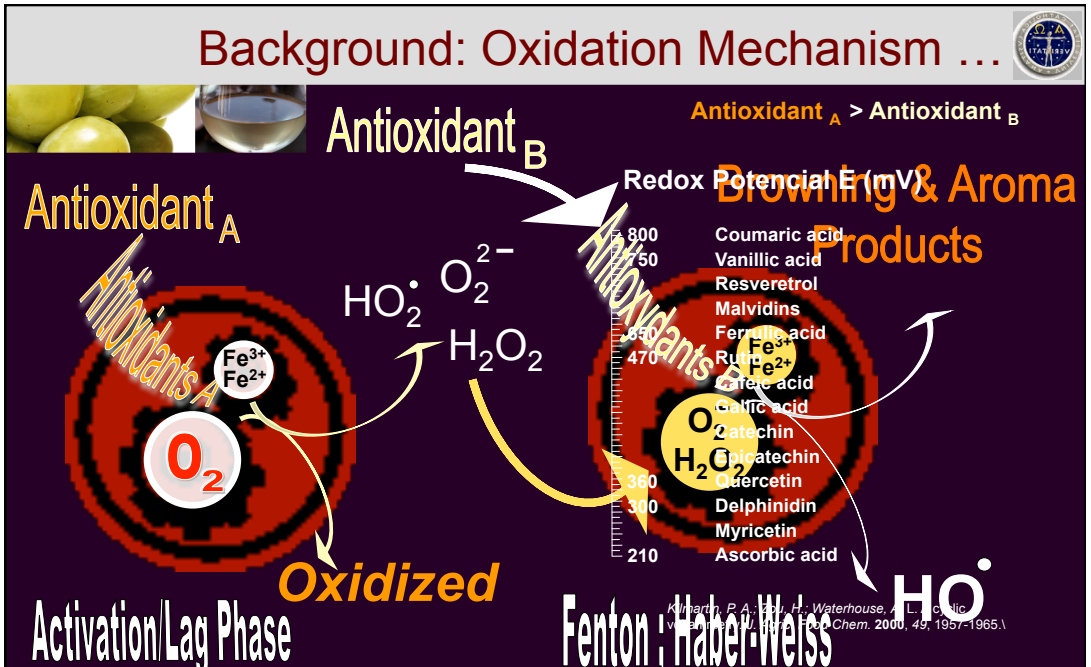
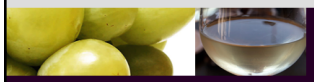
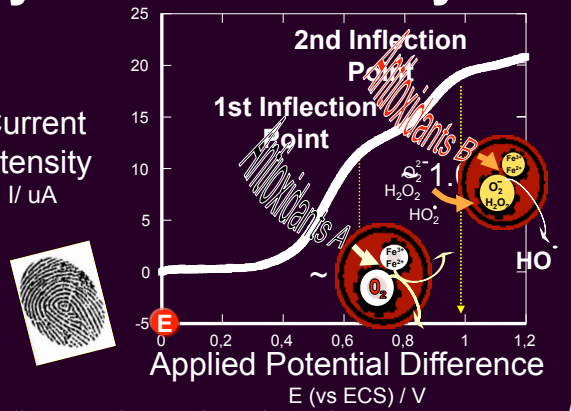

Background: Oxidation Mechanism …
Antioxidant A > Antioxidant B
Antioxidant B
Antioxidant A
Redox Potential E (mV)
800
750
650
470
360
300
210
Coumaric acid
Vanillic acid
Resveretrol
Malvidins
Ferrulic acid
Rutin
Caffeic acid
Gallic acid
Catechin
Epicatechin
Quercetin
Delphinidin
Myricetin
Ascorbic acid
Browning & Aroma Products
Antioxidants A
Antioxidants B
Fe^{3+} Fe^{2+}
O_2
$HO_2^{\bullet}$ O_2^{2-}
H_2O_2
Oxidized
Activation/Lag Phase
Fenton ; Haber-Weiss
$HO^{\bullet}$
Kilmartin, P.A.; Zou, H.; Waterhouse, A.L. ... J. Agric. Food Chem. 2000, 49, 1957-1965.



Cyclic Voltammetry



3 mm diameter glass carbon electrode
Scan Range: 100 mV / sec (diffusion)

Redox Potencial E (mV)

800	Coumaric acid
750	Vanillic acid
	Resveretrol
	Malvidins
650	Ferrulic acid
470	Rutin
	Cafeic acid
	Gallic acid
	Catechin
	Epicatechin
360	Quercetin
300	Delphinidin
	Myricetin
210	Ascorbic acid

Kilmartin, P. A.; Zou, H.; Waterhouse, A. L. A cyclic voltammetry. *J. Agric. Food Chem.* **2000**, *49*, 1957-1965.

Experimental Design : Sample Preparation

- **Forced Aging Protocol**

- Group I -
pH= 3.2 ; [SO2]free =12 mg/L ; [O2]= 1.0 mg/L

Treatment I	Treatment II	Treatment III	Treatment IV
pH = 3.2	SO_2 (free) = 50 mg/L	O_2 dissolved = 8 mg/L	pH = 4.2

Stored @ T = 15 ºC ; @ T = 45 ºC

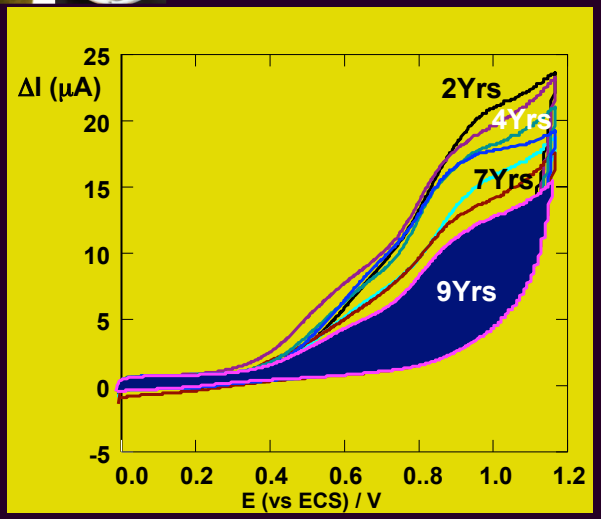
Sensory and Chemical analysis

- **Normal Aged**

Different Vintages (*n*=24) Age 1-20 years Old
- Group II -

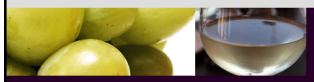
- **Oxygen Permeability : Cork Stopper**

Cyclic Voltammetry: Normal Aged Wines

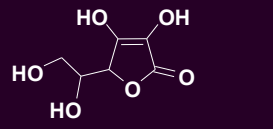


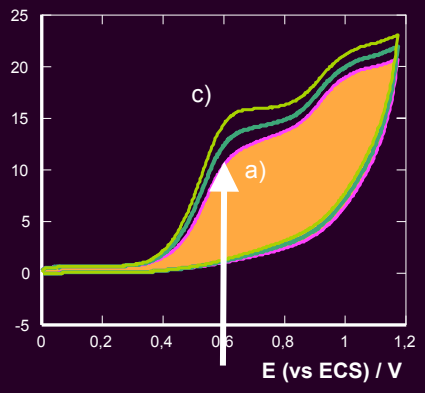
QtCarv_9Yrs
Borba_2Yrs
Douro_4Yrs
Douro_6Yrs
FernP_7Yrs
Espor_4Yrs
Murça_2Yrs

Cyclic Voltammetry: Antioxidants Impact

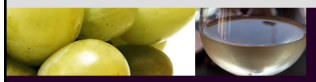


ΔI (μA)



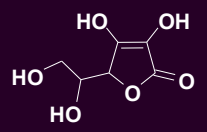


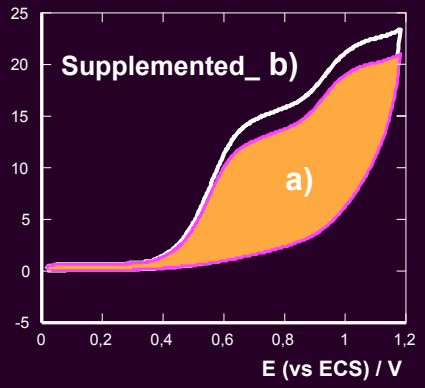
Ip1 ± s (μA)	Ip2 ± s (μA)	
13.7 ± 0.1	21.0 ± 0.2	a) white wine sample
15.3 ± 0.1	22.1 ± 0.1	b) white wine sample with 25 mg/ L of ascorbic acid
17.3 ± 0.1	23.4 ± 0.3	c) white wine sample with 50 mg/ L of ascorbic acid



SO_2

&

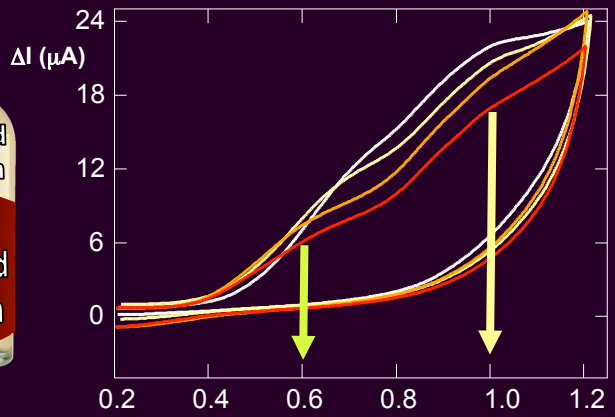




Ip1 ± s (μA)	Ip2 ± s (μA)	
13.7 ± 0.1	21.0 ± 0.2	a) white wine sample
16.0 ± 0.1	23.4 ± 0.2	b) white wine sample with 20 mg/ L of free sulphur dioxide + 25 mg/ L of ascorbic acid.

Cyclic Voltammetry: Oxygen Impact

Oxygen Saturation ; T= 45 °C

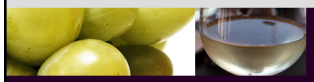


t= 0 days

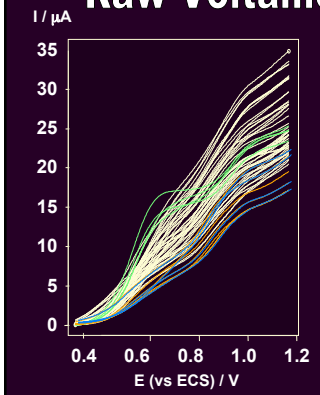
t= 15 days

t= 30 days

t= 60 days



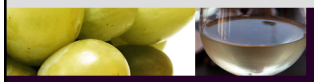
Raw Voltametry

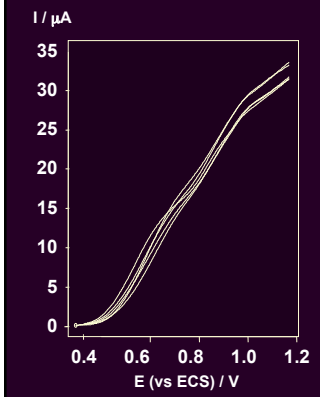


All Data Points Contains

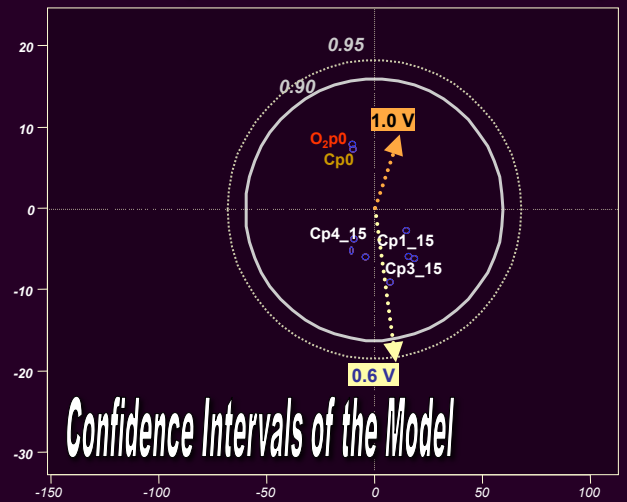
- **Quantitative**
- **Information**
- **Qualitative**

Data Treatment : Shelf Life Control Chart

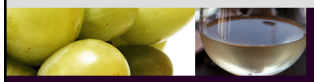


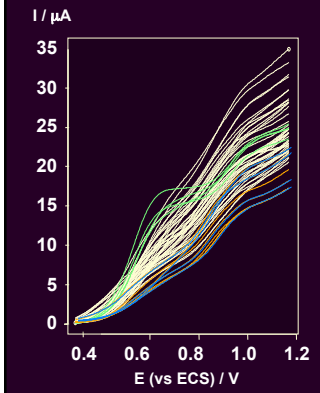


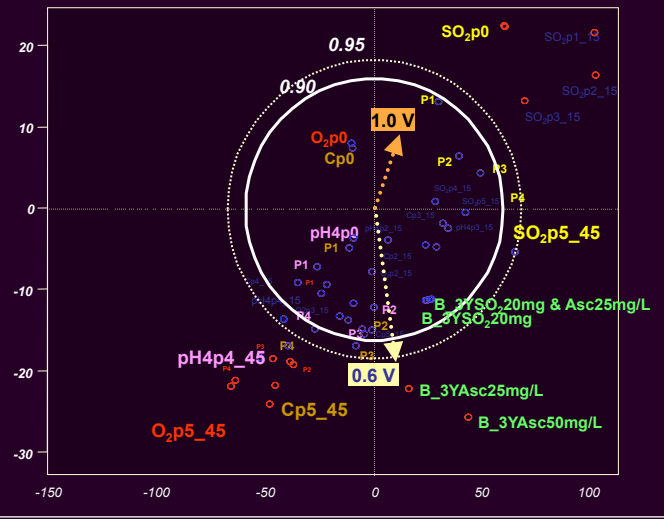
R-SVD Loadings Directions: High Low Reactivity



Confidence Intervals of the Model

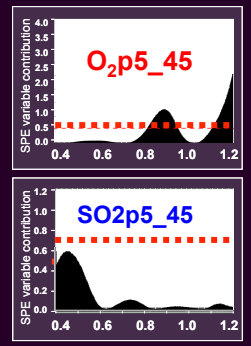


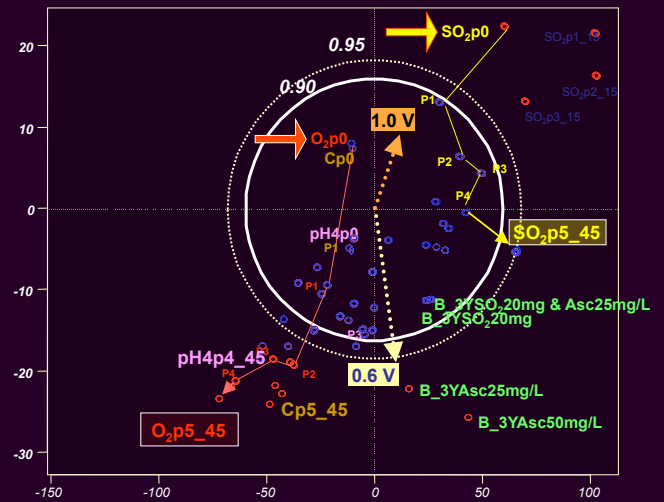


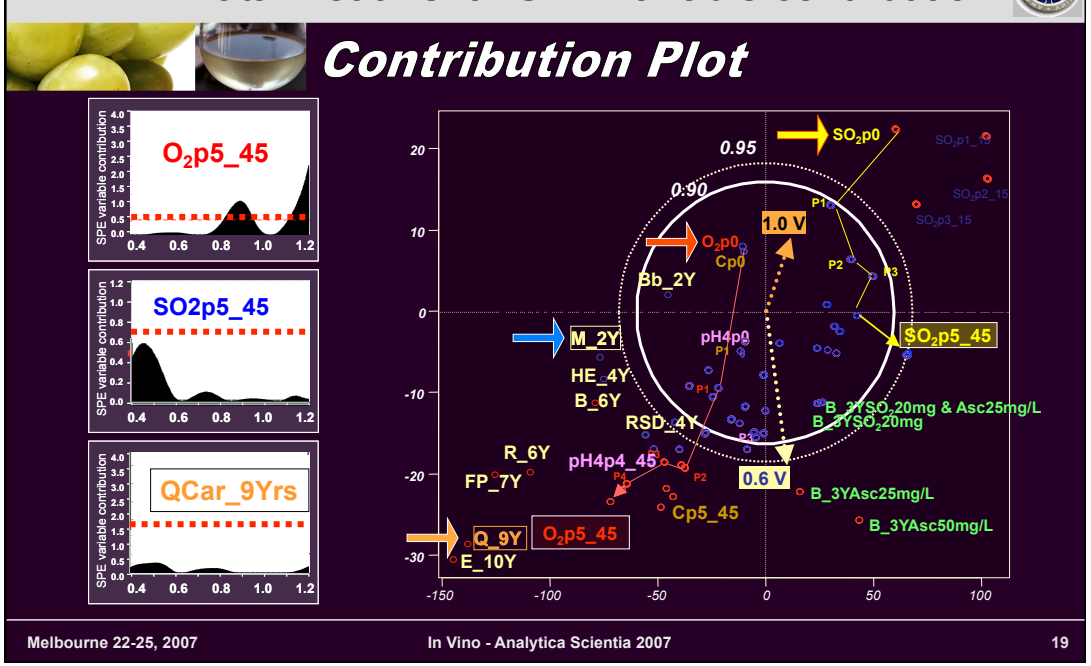


Data Treatment : SPE variable contribution

Contribution Plot






Contribution Plot
O2p5_45
SO2p5_45
QCar_9Yrs
SPE variable contribution
SO2p0
0.95
0.90
1.0 V
0.6 V
O2p0
Cp0
Bb_2Y
M_2Y
HE_4Y
B_6Y
RSD_4Y
R_6Y
FP_7Y
pH4p0
pH4p4_45
Cp5_45
O2p5_45
Q_9Y
E_10Y
SO2p5_45
B_3YSO2_20mg & Asc25mg/L
B_3YSO2_20mg
B_3YAsc25mg/L
B_3YAsc50mg/L
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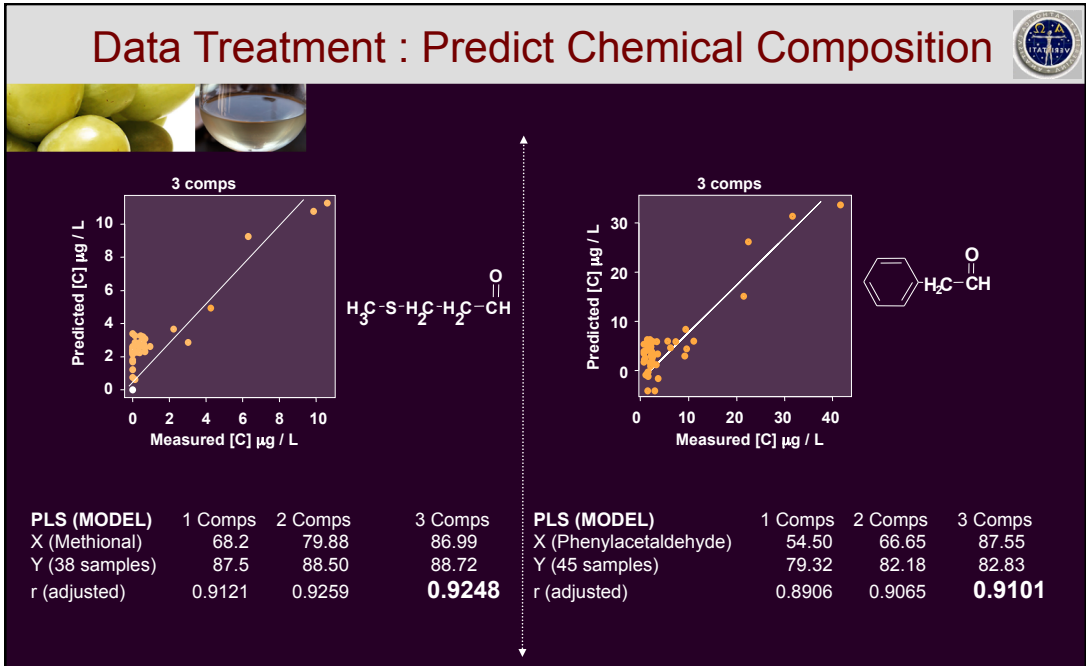
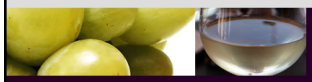

Data Treatment : Predict Chemical Composition
3 comps
Predicted [C] µg / L
Measured [C] µg / L
PLS (MODEL) 1 Comps 2 Comps 3 Comps
X (Methional) 68.2 79.88 86.99
Y (38 samples) 87.5 88.50 88.72
r (adjusted) 0.9121 0.9259 0.9248
3 comps
Predicted [C] µg / L
Measured [C] µg / L
PLS (MODEL) 1 Comps 2 Comps 3 Comps
X (Phenylacetaldehyde) 54.50 66.65 87.55
Y (45 samples) 79.32 82.18 82.83
r (adjusted) 0.8906 0.9065 0.9101



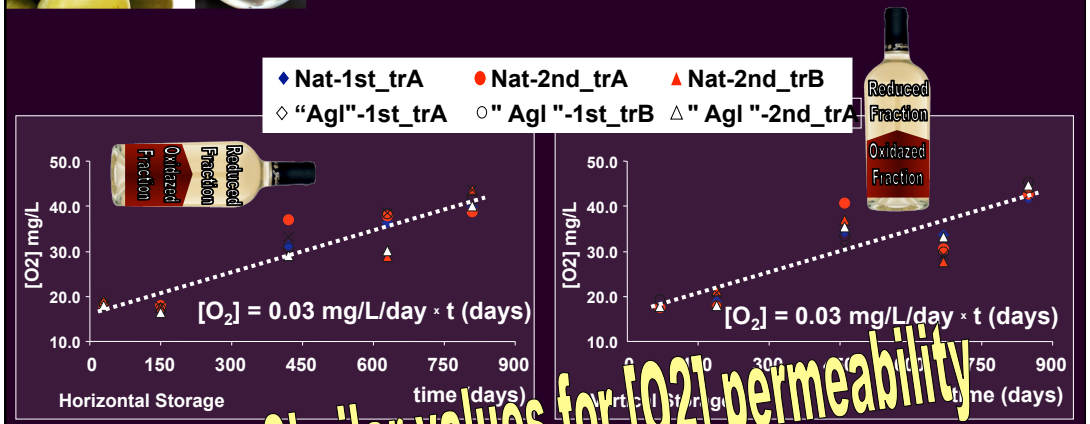
Tartaric Acid ~ pH = 2.5

Na_2SO_3 ~ SO_2 free > 200 mg/L

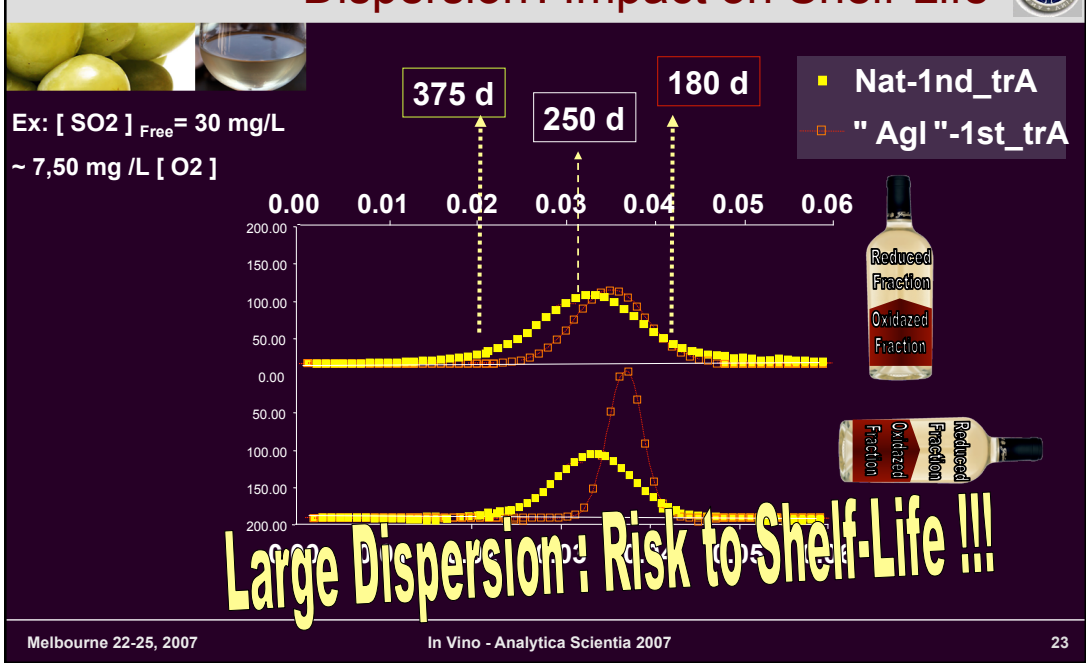
2000L H2O

$$2\ SO_3^{2-} + O_2 \longleftrightarrow 2\ SO_4^{-2}$$

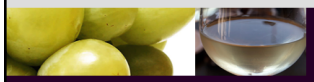
Oxygen Permeability : Storage Position



Similar values for [O2] permeability



Conclusions



In order to optimize shelf-life three conditions must be addressed and become standardized for industry application:

- Dissolved oxygen must be Controlled;
- Both the quantity and quality of antioxidants present in solution need to be Evaluated;
- Thirdly the permeability of the stopper need to be Provided.

Acknowledgments

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V. Lopes