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Impact of Oxygen on Wine Quality

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Oxygen : A management tool for "Sensory Quality"

- "Shelf-life" : Development of a fingerprinting strategy capable of evaluate the "oxidation status" of wines

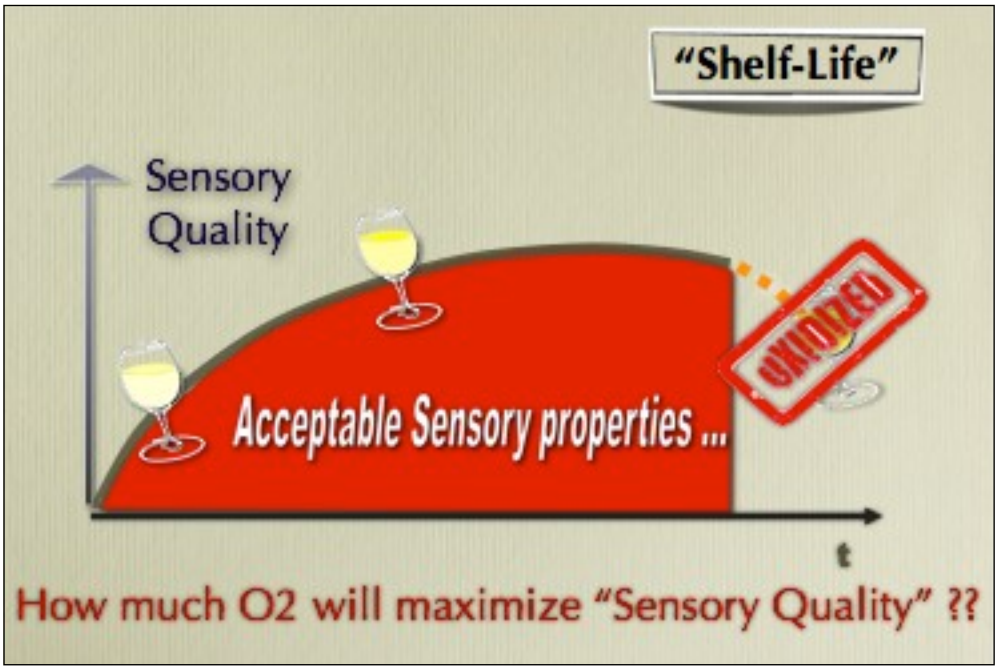
- Chemical mechanisms : Impact of Oxygen and Temperature on the flavour by:

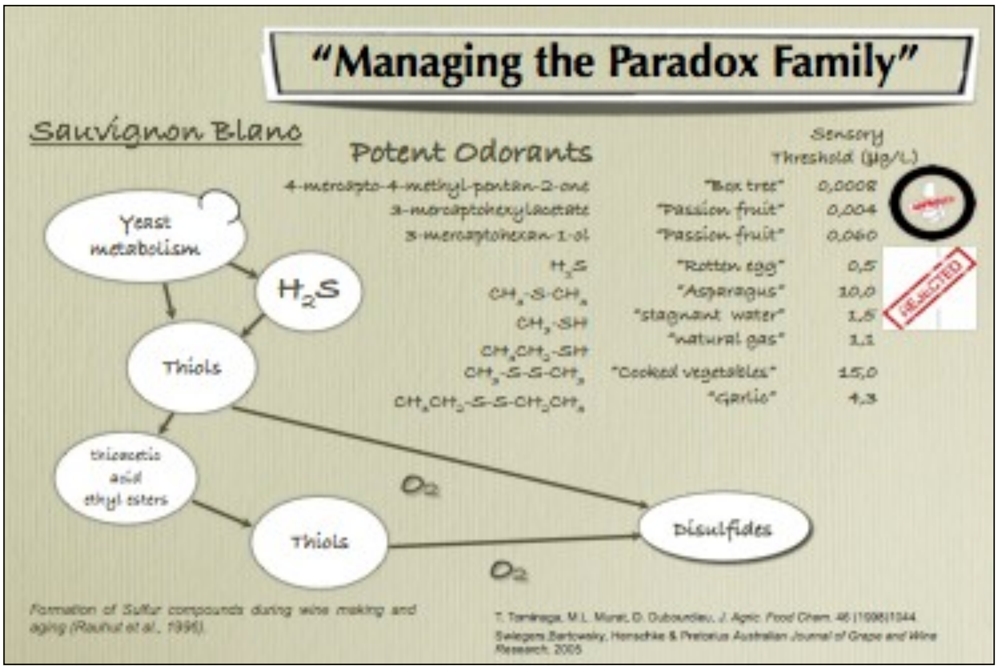
  - Applying empirical kinetic models of the key-compounds to monitor the impact of O_2 and Temperature;

  - Building a "wine feature database" from the target compounds in order to predict/classify the effect of temperature and O_2 using the kinetic models

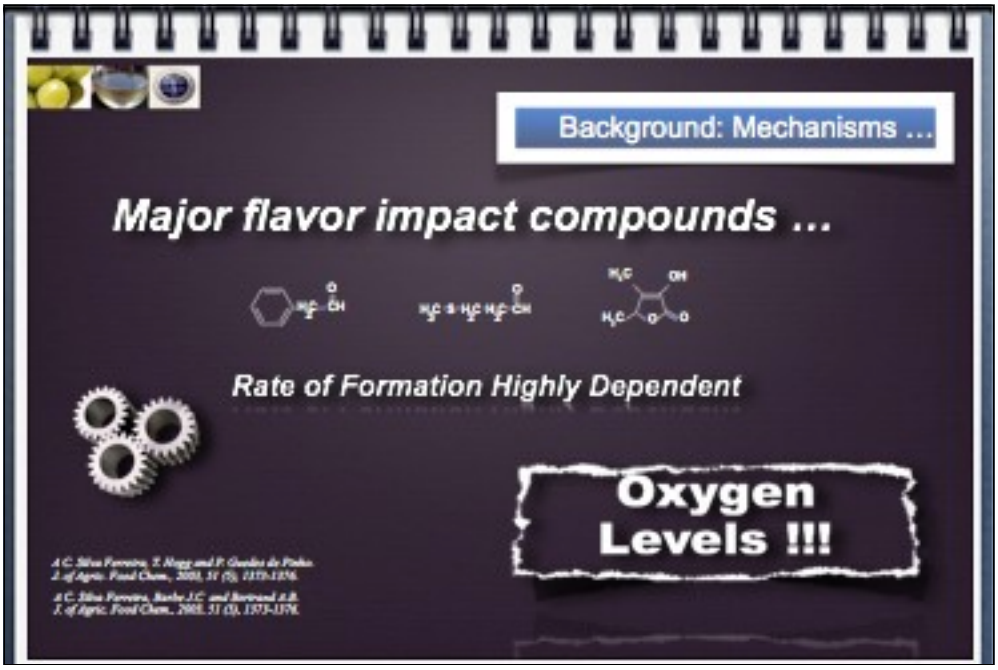
Complexity

$$\text{Wine}_{\text{glass}} = \int_{\text{pruning}}^{\text{harvest}} \text{vine} \times \int_{\text{juice}}^{\text{fermented must}} \text{yeast} \times \int_{\text{finished wine}}^{\text{consumption}} \text{aging}$$

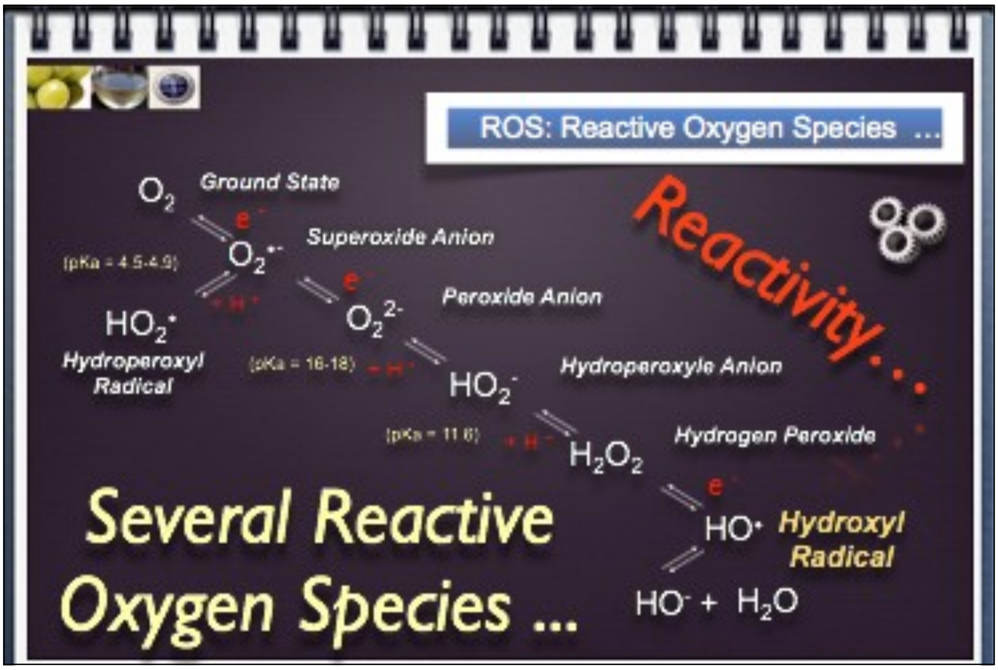

"Shelf-Life"
Sensory Quality
Acceptable Sensory properties ...
OXIDIZED
t
How much O2 will maximize "Sensory Quality" ??


"Managing the Paradox Family"
Sauvignon Blanc
Potent Odorants
Sensory Threshold (µg/L)
4-mercapto-4-methyl-pentan-2-one "Box tree" 0,0008
3-mercaptohexylacetate "Passion fruit" 0,004
3-mercaptohexan-1-ol "Passion fruit" 0,060
H2S "Rotten egg" 0,5
CH3-S-CH3 "Asparagus" 10,0
CH3-SH "stagnant water" 1,5
CH3CH2-SH "natural gas" 1,1
CH3-S-S-CH3 "Cooked vegetables" 15,0
CH3CH2-S-S-CH2CH3 "Garlic" 4,3
REJECTED
Yeast metabolism
H2S
Thiols
thioacetic acid ethyl esters
Thiols
O2
O2
Disulfides
Formation of Sulfur compounds during wine making and aging (Rauhut et al., 1996).
T. Tominaga, M.L. Murat, D. Dubourdieu, J. Agric. Food Chem. 46 (1998) 1044
Swiegers Bartowsky, Henschke & Pretorius Australian Journal of Grape and Wine Research. 2005

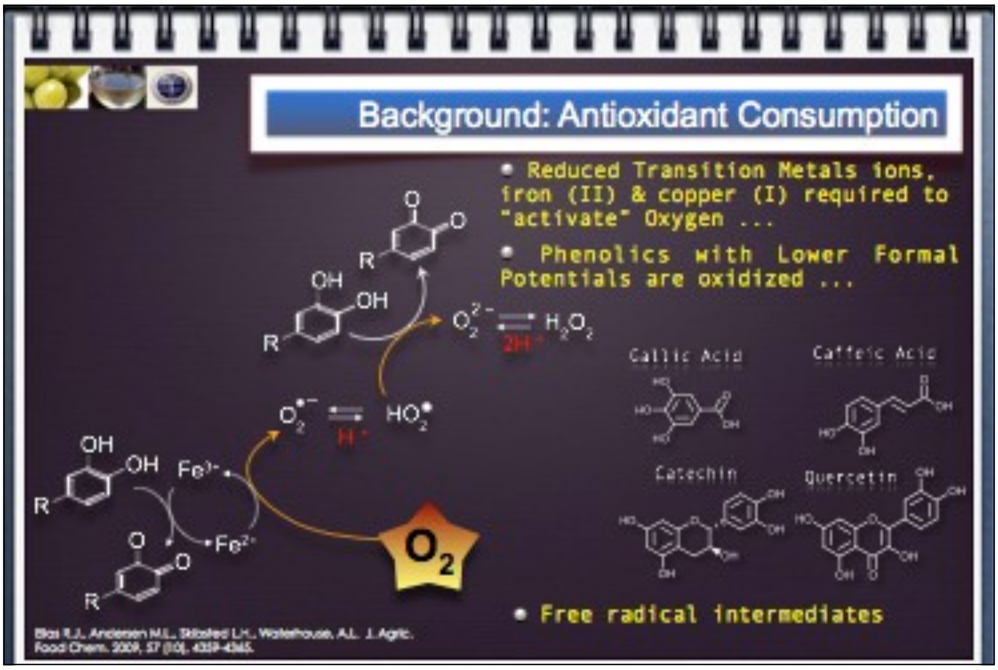

" Key-Odorants"
Phenylacetaldehyde
Methional
Sotolon
White Wine
off - Flavor
Sotolon
Porto, Sherry
Madeira Wines
positive - Flavor



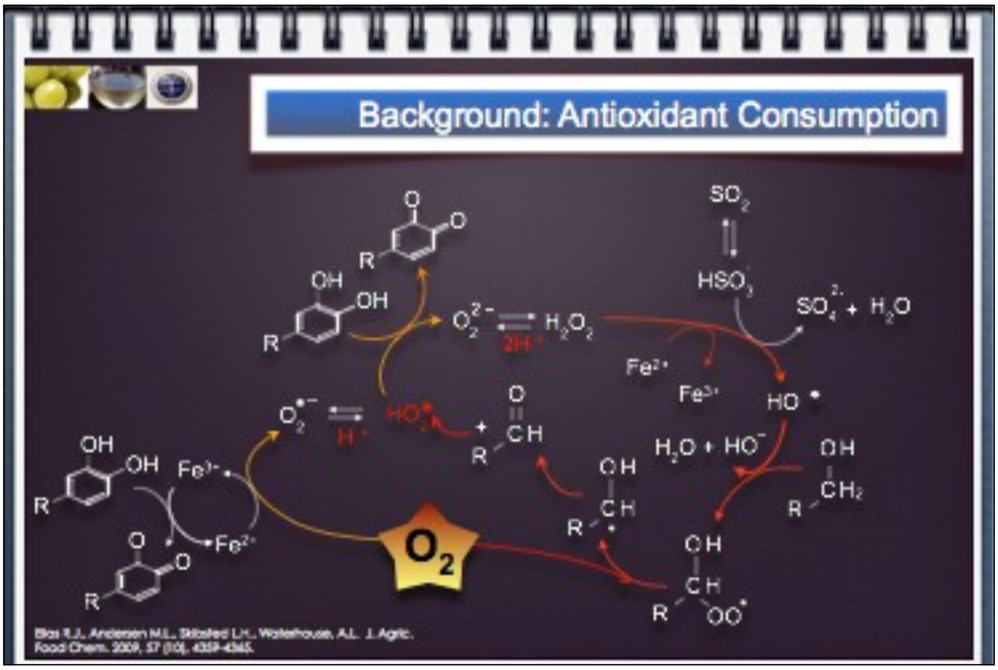
Background: Mechanisms ...
Major flavor impact compounds ...
Rate of Formation Highly Dependent
Oxygen
Levels !!!

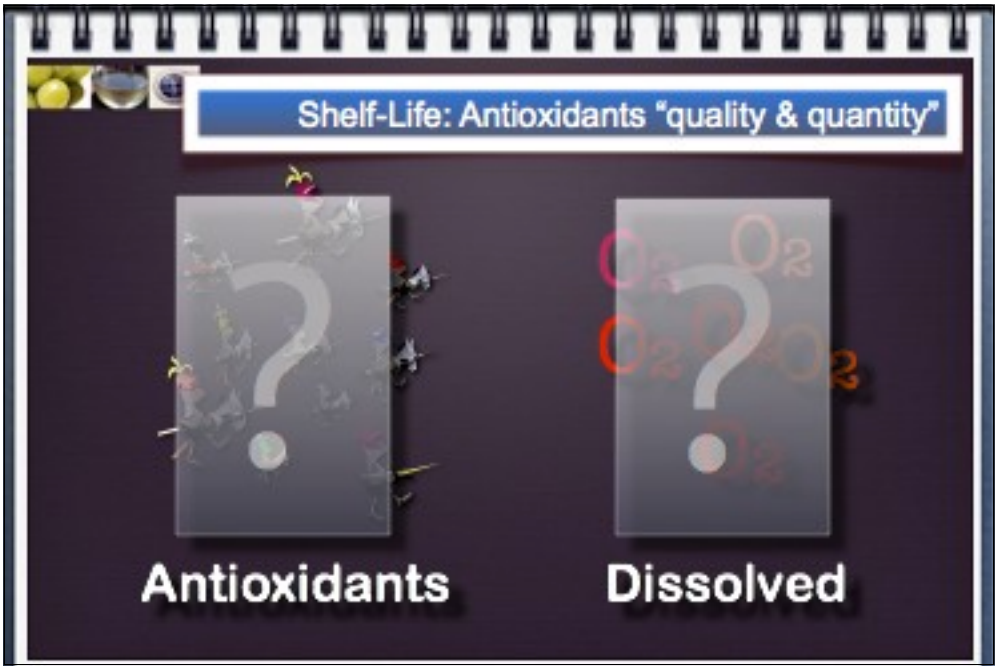


ROS: Reactive Oxygen Species ...
O_2 Ground State
Superoxide Anion
(pKa = 4.5-4.9)
$HO_2^•$
Hydroperoxyl Radical
Peroxide Anion
(pKa = 16-18)
HO_2^-
Hydroperoxyle Anion
(pKa = 11.6)
H_2O_2
Hydrogen Peroxide
HO• Hydroxyl Radical
$HO^- + H_2O$
Reactivity...
Several Reactive
Oxygen Species ...

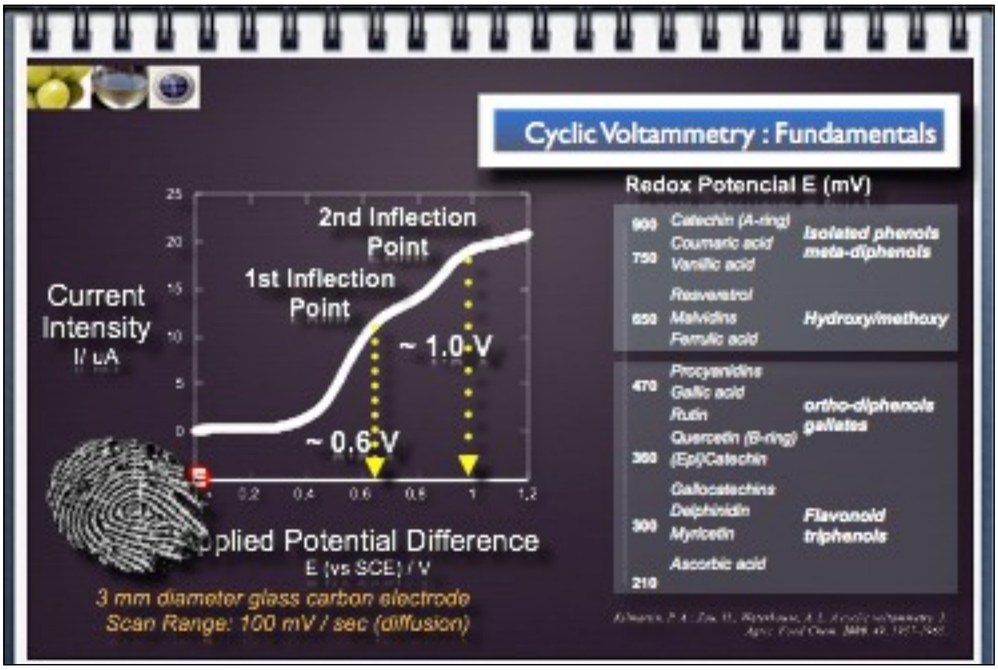


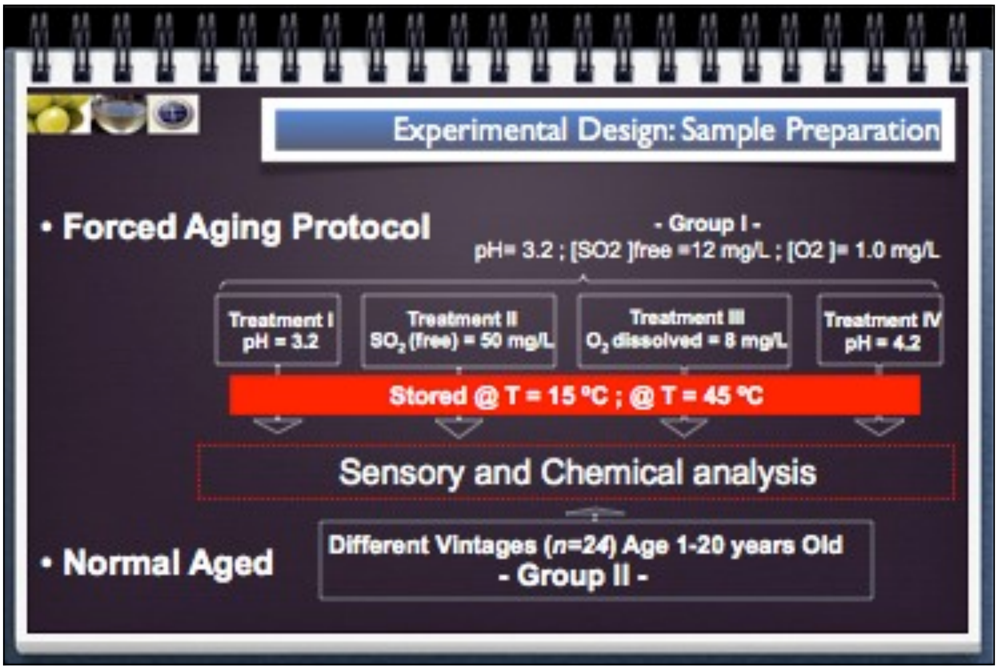
Background: Antioxidant Consumption
• Reduced Transition Metals ions, iron (II) & copper (I) required to "activate" Oxygen ...
• Phenolics with Lower Formal Potentials are oxidized ...
Gallic Acid
Caffeic Acid
Catechin
Quercetin
Fe^{3+}
Fe^{2+}
O_2
• Free radical intermediates

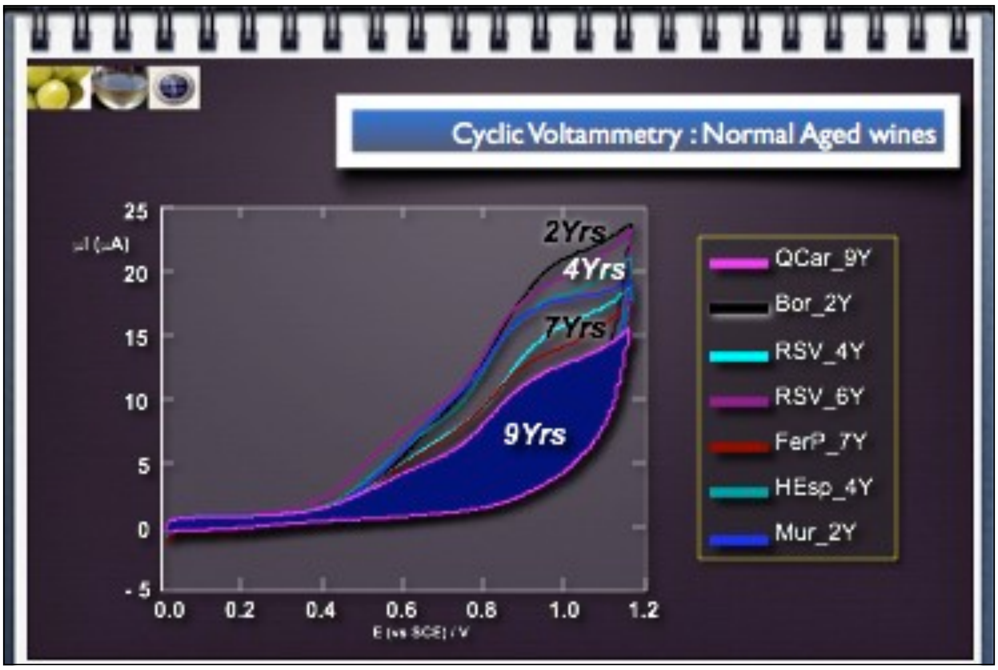

Background: Antioxidant Consumption
Elias R.J., Andersen M.L., Skibsted L.H., Waterhouse, A.L. J. Agric. Food Chem. 2009, 57 (10), 4359-4365.

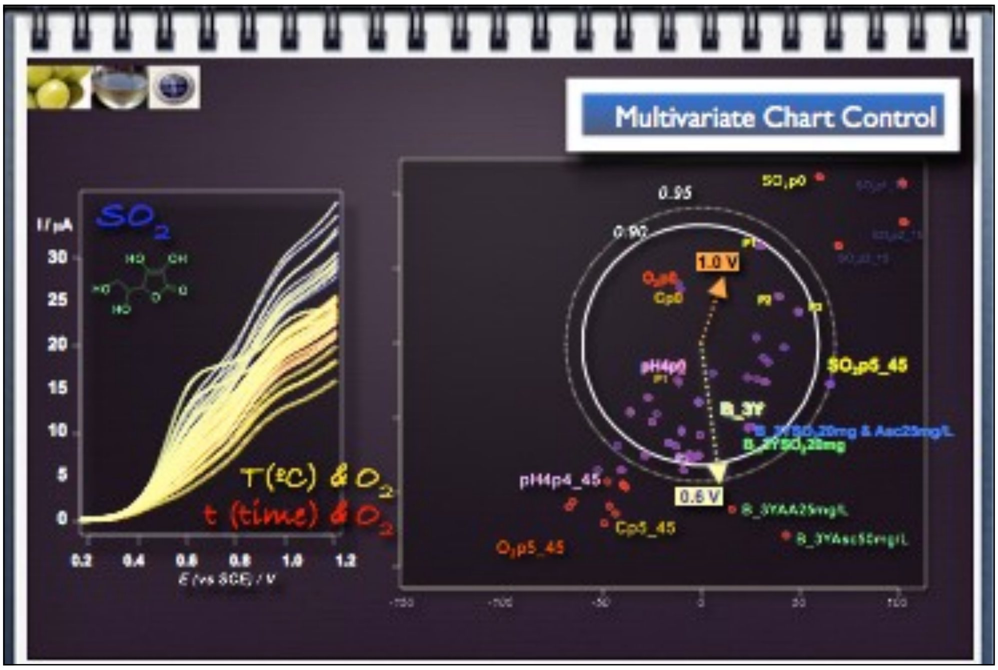

Shelf-Life: Antioxidants “quality & quantity”
Antioxidants
Dissolved

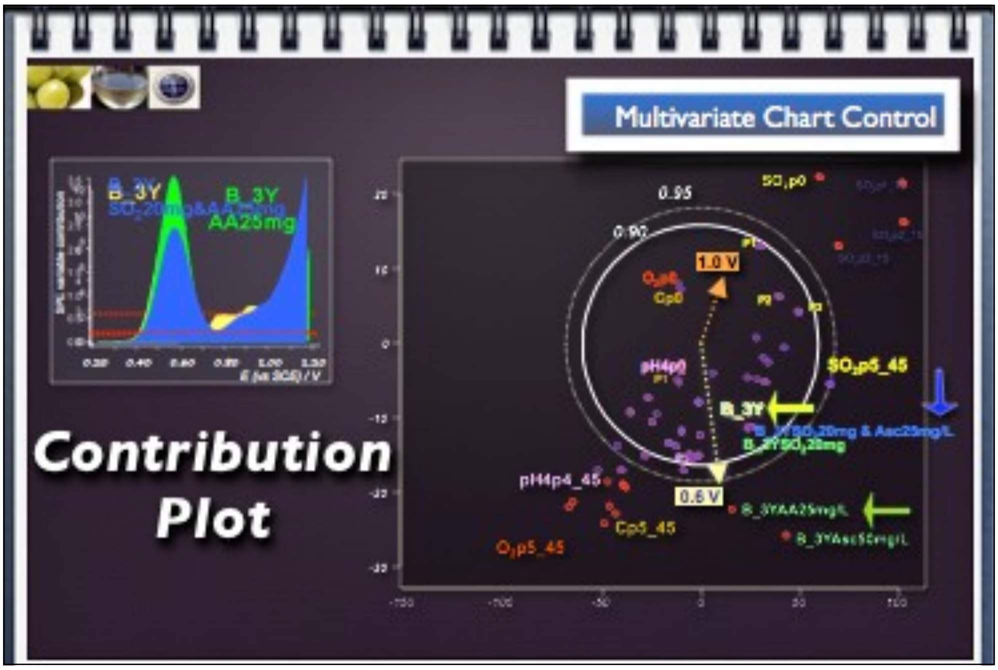

Tools

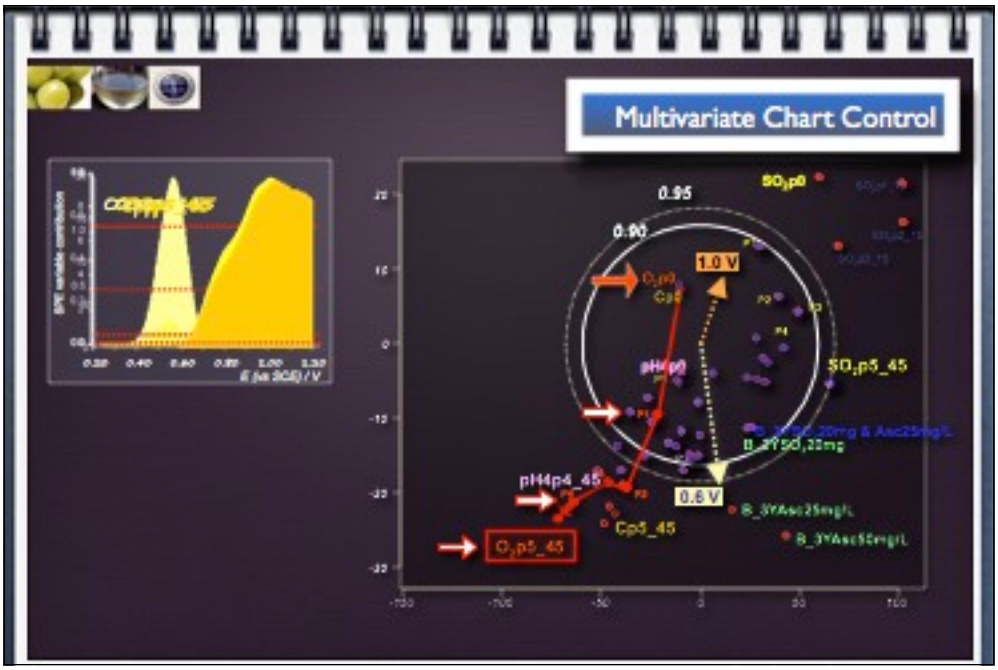

Cyclic Voltammetry : Fundamentals
Current Intensity I/ uA
2nd Inflection Point
1st Inflection Point
~ 1.0 V
~ 0.6 V
Applied Potential Difference
E (vs SCE) / V
3 mm diameter glass carbon electrode
Scan Range: 100 mV / sec (diffusion)
Redox Potencial E (mV)
900 Catechin (A-ring)
Coumaric acid
750 Vanillic acid
Isolated phenols meta-diphenols
Resveratrol
650 Malvidins
Ferrulic acid
Hydroxy/methoxy
Procyanidins
470 Gallic acid
Rutin
Quercetin (B-ring)
360 (Epi)Catechin
ortho-diphenols gallates
Gallocatechins
Delphinidin
300 Myricetin
Ascorbic acid
210
Flavonoid triphenols

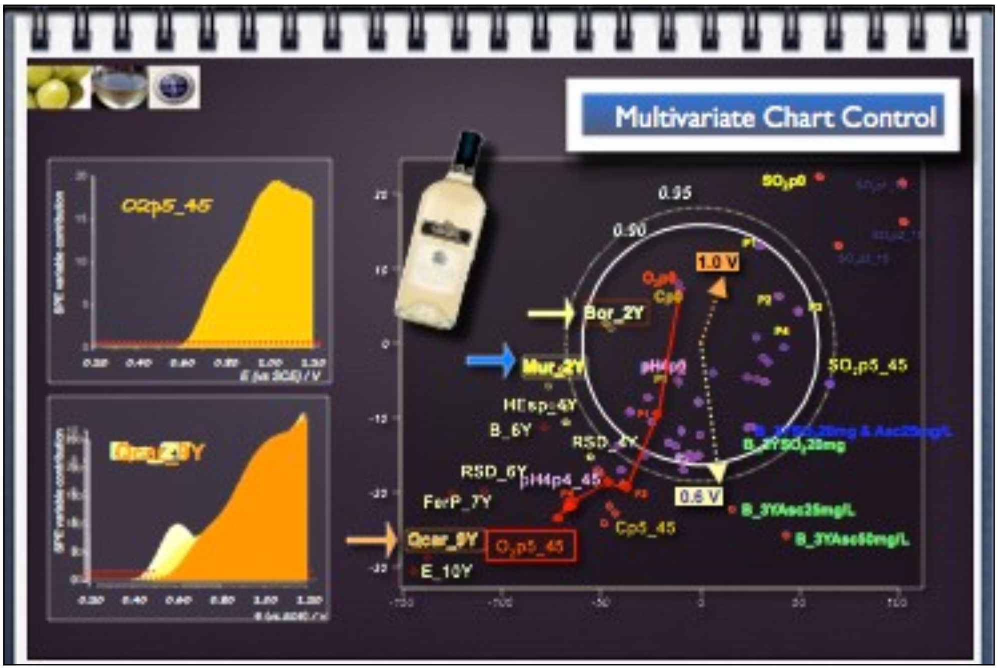

Experimental Design: Sample Preparation
• Forced Aging Protocol
- Group I -
pH= 3.2 ; [SO2]free =12 mg/L ; [O2]= 1.0 mg/L
Treatment I pH = 3.2
Treatment II SO2 (free) = 50 mg/L
Treatment III O2 dissolved = 8 mg/L
Treatment IV pH = 4.2
Stored @ T = 15 °C ; @ T = 45 °C
Sensory and Chemical analysis
• Normal Aged
Different Vintages (n=24) Age 1-20 years Old
- Group II -

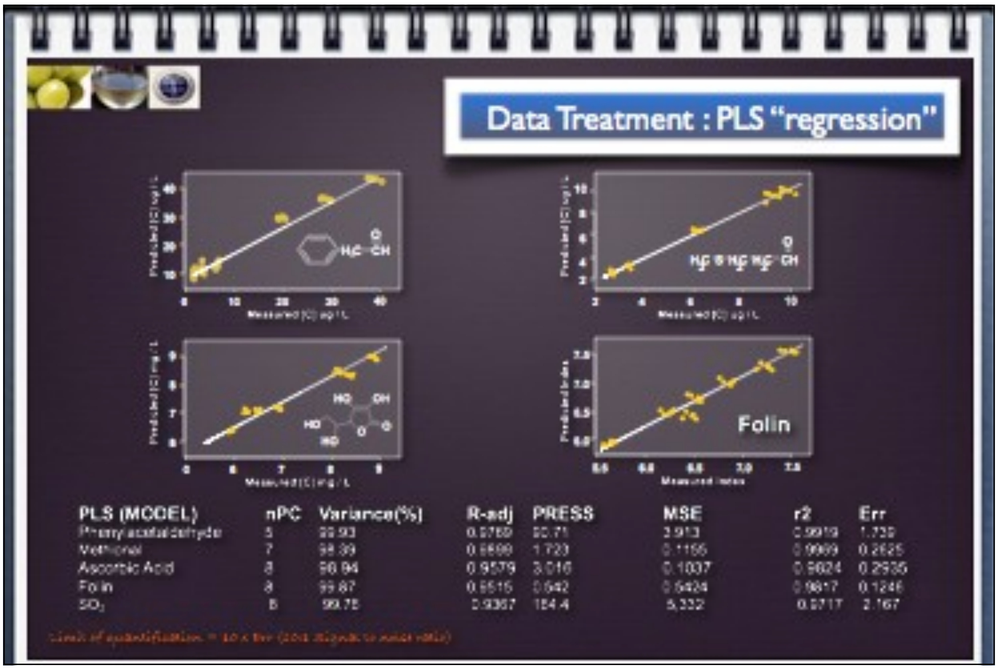

Cyclic Voltammetry : Normal Aged wines
I (uA)
E (vs SCE) / V
2Yrs
4Yrs
7Yrs
9Yrs
QCar_9Y
Bor_2Y
RSV_4Y
RSV_6Y
FerP_7Y
HEsp_4Y
Mur_2Y


Multivariate Chart Control
SO_2
I / µA
E (vs SCE) / V
T(ºC) & O_2
t (time) & O_2
0.95
0.90
1.0 V
0.8 V
SO_2p0
SO_2p5_45
pH4p0
pH4p4_45
Cp0
Cp5_45
O_2p5_45
B_3Y
B_3YSO$_2$20mg & Asc25mg/L
B_3YSO$_2$20mg
B_3YAA25mg/L
B_3YAsc50mg/L

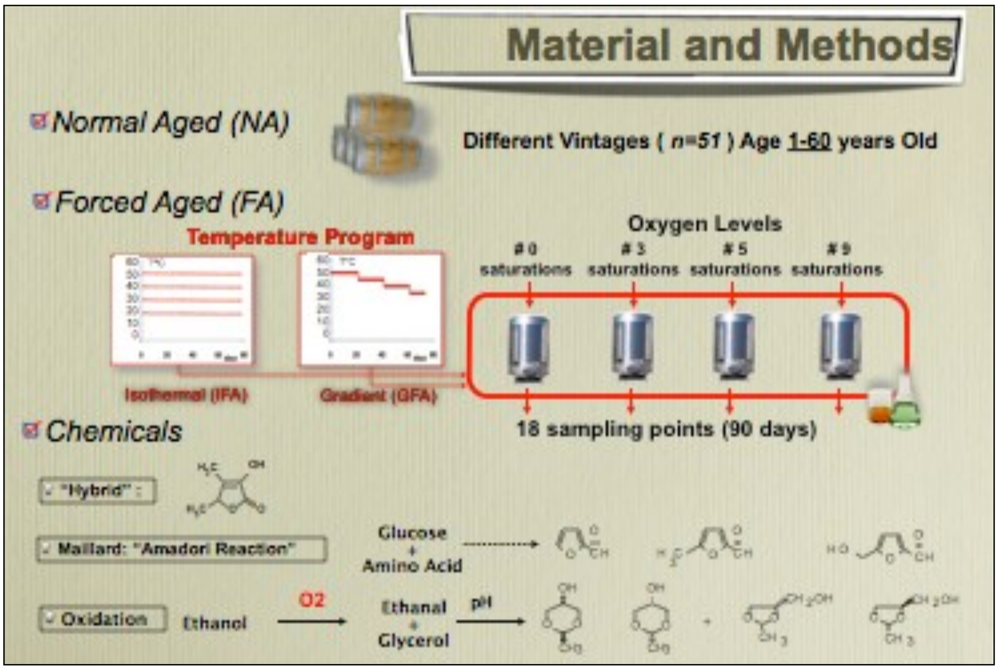

Multivariate Chart Control
B_3Y
B_3Y
AA25mg
Contribution Plot
0.95
0.90
1.0 V
0.8 V
SO_2p0
SO_2p5_45
pH4p0
pH4p4_45
Cp0
Cp5_45
O_2p5_45
B_3Y
B_3YSO$_2$20mg & Asc25mg/L
B_3YSO$_2$20mg
B_3YAA25mg/L
B_3YAsc50mg/L


Multivariate Chart Control
E (vs SCE) / V
0.95
0.90
1.0 V
0.8 V
SO_2p0
SO_2p5_45
pH4p0
pH4p4_45
O_2p0
Cp0
Cp5_45
O_2p5_45
B_3YSO$_2$20mg & Asc25mg/L
B_3YSO$_2$20mg
B_3YAsc25mg/L
B_3YAsc50mg/L

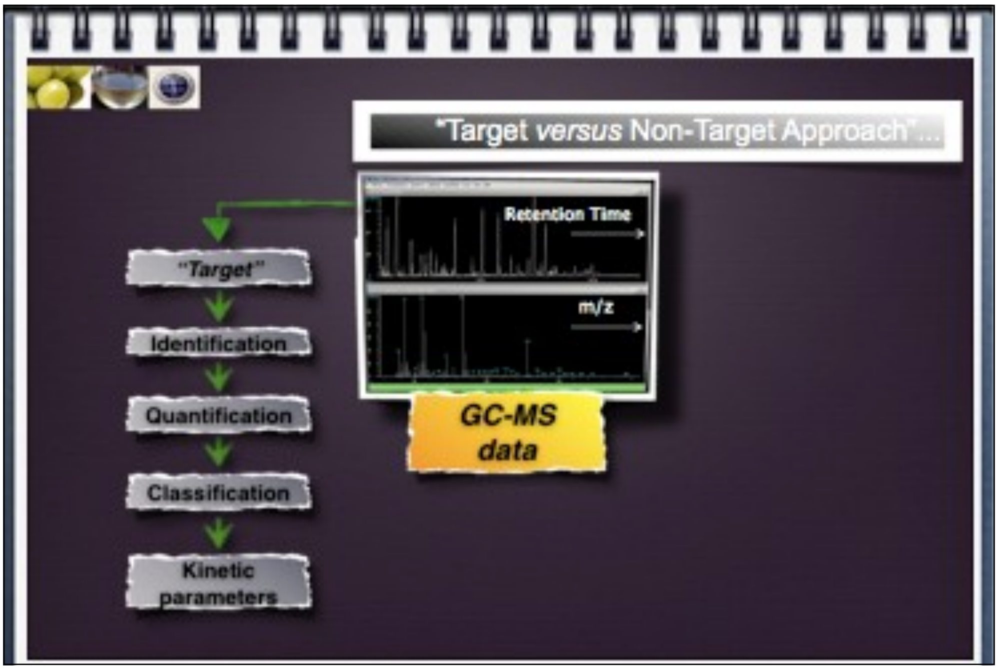




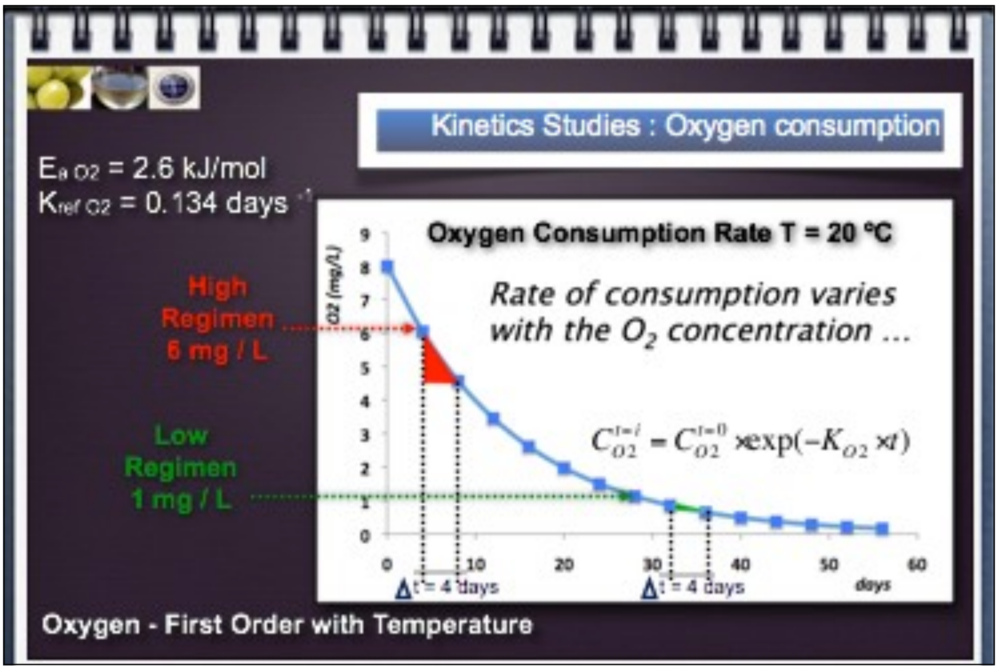
PLS (MODEL)	nPC	Variance(%)	R-adj	PRESS	MSE	r2	Err
Phenylacetaldehyde	5	99.93	0.9769	90.71	3.913	0.9919	1.729
Methional	7	98.39	0.9898	1.720	0.1156	0.9969	0.2625
Ascorbic Acid	8	98.94	0.9579	3.016	0.1037	0.9824	0.2935
Folin	8	99.87	0.9515	0.642	0.5424	0.9817	0.1246
SO_2	6	99.75	0.9367	184.4	5.332	0.9717	2.167



Material and Methods
Normal Aged (NA)
Different Vintages (n=51) Age 1-60 years Old
Forced Aged (FA)
Temperature Program
Oxygen Levels
0 saturations
3 saturations
5 saturations
9 saturations
Isothermal (IFA)
Gradient (GFA)
18 sampling points (90 days)
Chemicals
"Hybrid" :
Maillard: "Amadori Reaction"
Glucose + Amino Acid
Oxidation
Ethanol
O2
Ethanal + Glycerol
pH



"Target versus Non-Target Approach"...
Retention Time
m/z
GC-MS data
"Target"
Identification
Quantification
Classification
Kinetic parameters

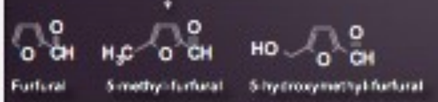


Kinetics Studies : Oxygen consumption
Ea O2 = 2.6 kJ/mol
Kref O2 = 0.134 days -1
High Regimen 6 mg / L
Low Regimen 1 mg / L
Oxygen Consumption Rate T = 20 °C
Rate of consumption varies with the O2 concentration ...
$C_{O2}^{t=i} = C_{O2}^{t=0} \times \exp(-K_{O2} \times t)$
O2 (mg/L)
days
Δt = 4 days
Δt = 4 days
Oxygen - First Order with Temperature

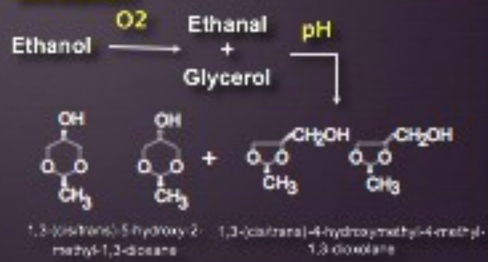
Kinetics Studies : Furfurals & Acetals

Maillard : Amadori Reaction

Glucose + Amino Acid



Oxidation



$$C(t) = C_{eq} - (C_{eq} - C_0)\,e^{-\int_0^t k_{app}\,dt}$$

Ea; k - First Order reversible with Temperature

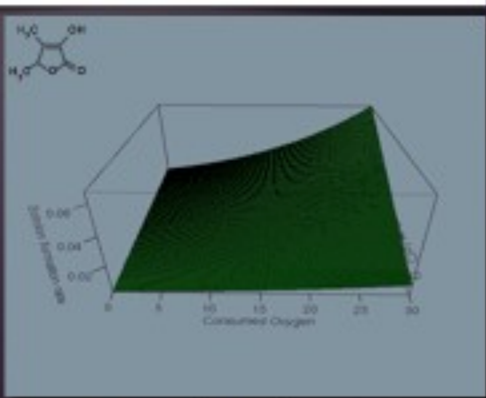
$E_{a\ furfural}$ = 143.1 kJ/mol
$K_{ref\ furfural}$ = 0.0009 days $^{-1}$

$E_{a\ dioxane}$ = 32.5 kJ/mol
$K_{ref\ dioxane}$ = 0.0011 days $^{-1}$

Kinetics Studies : Sotolon Rate of Formation

$$C_{Sot}^{t=i} = C_{Sot}^{t=0} + r_{Sot} \times t$$
$$r_{Sot} = C_{O_2}^{Cons} \cdot k_{ref}^{Sot} \cdot \exp\left[\frac{E_a^{Sot}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

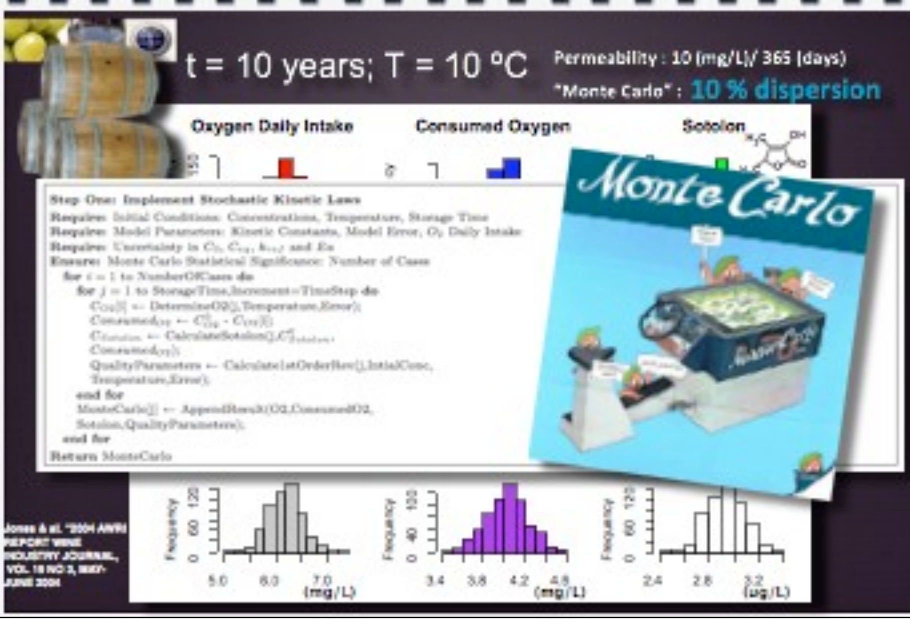
$E_{a\ sot}$ = 38 kJ/mol
$K_{ref\ sot}$ = 0.012 days $^{-1}$



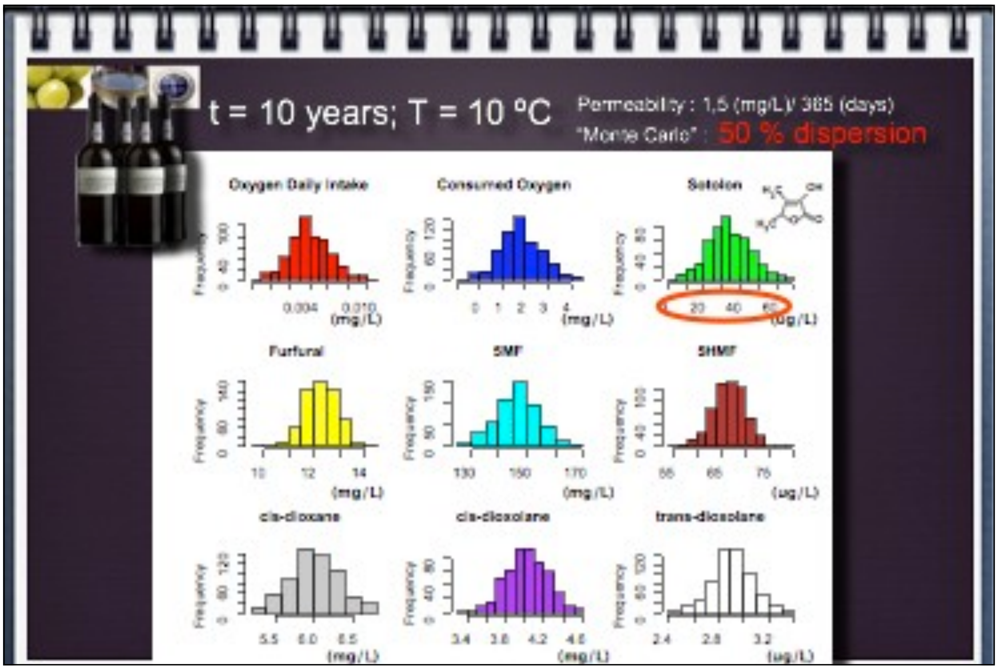
Sotolon Rate of Formation
- directly proportional to oxygen consumption rate;
- exponential dependent on storage temperature.

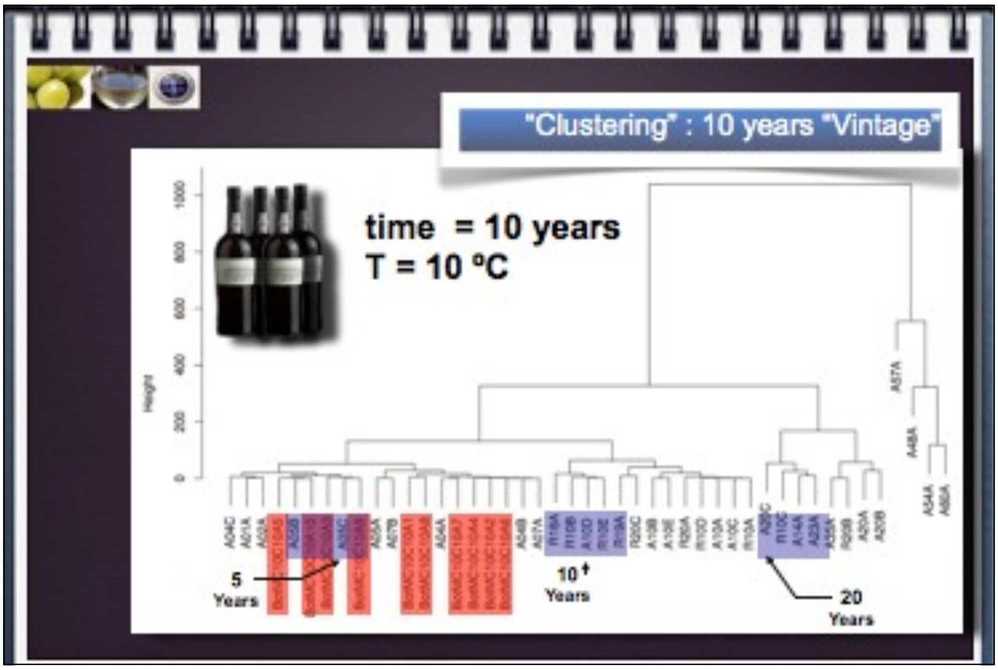
t = 10 years; T = 10 °C

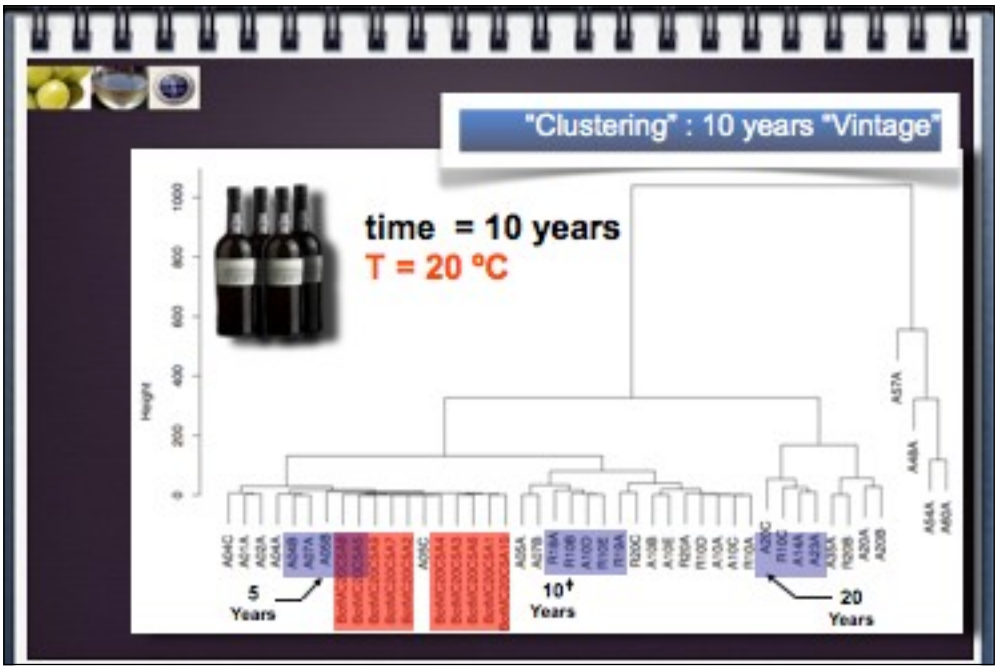
Permeability : 10 (mg/L)/ 365 (days)
"Monte Carlo" : 10 % dispersion

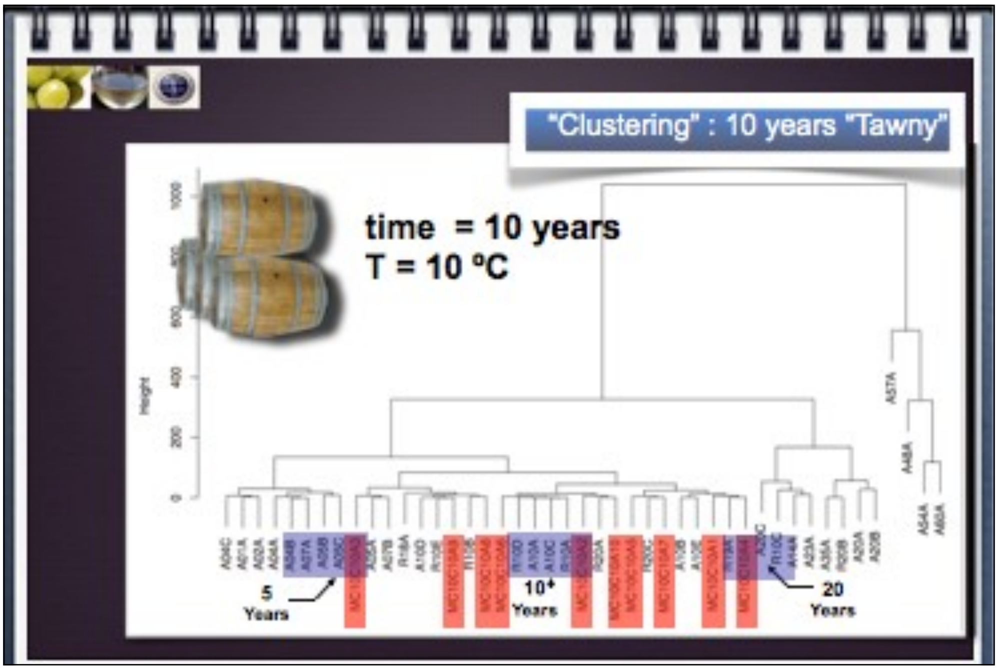


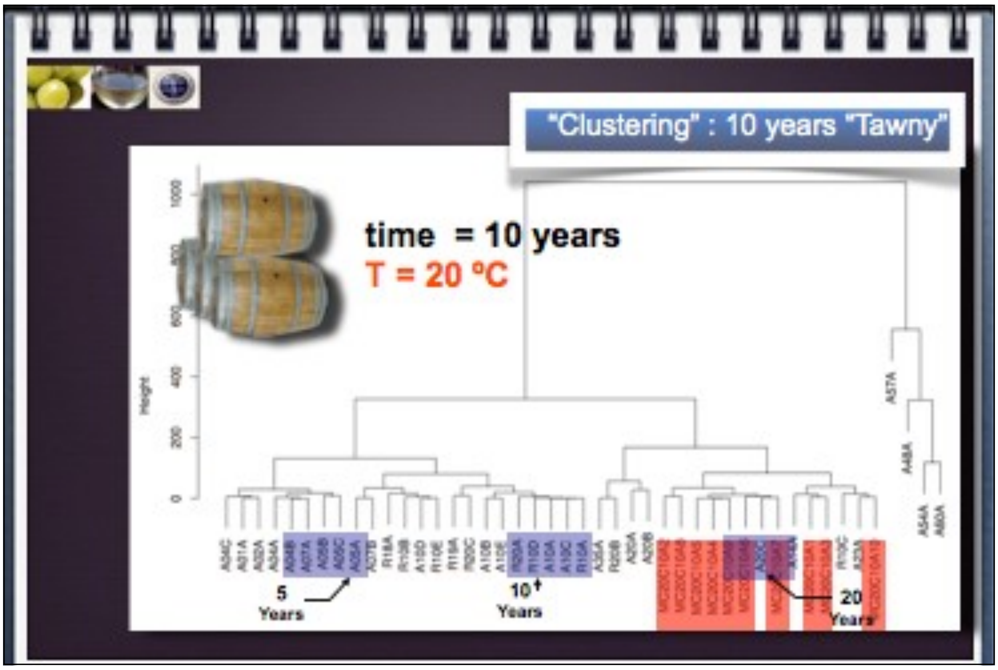
Jones & al. "2004 AWRI REPORT WINE INDUSTRY JOURNAL, VOL. 19 NO 3, MAY-JUNE 2004

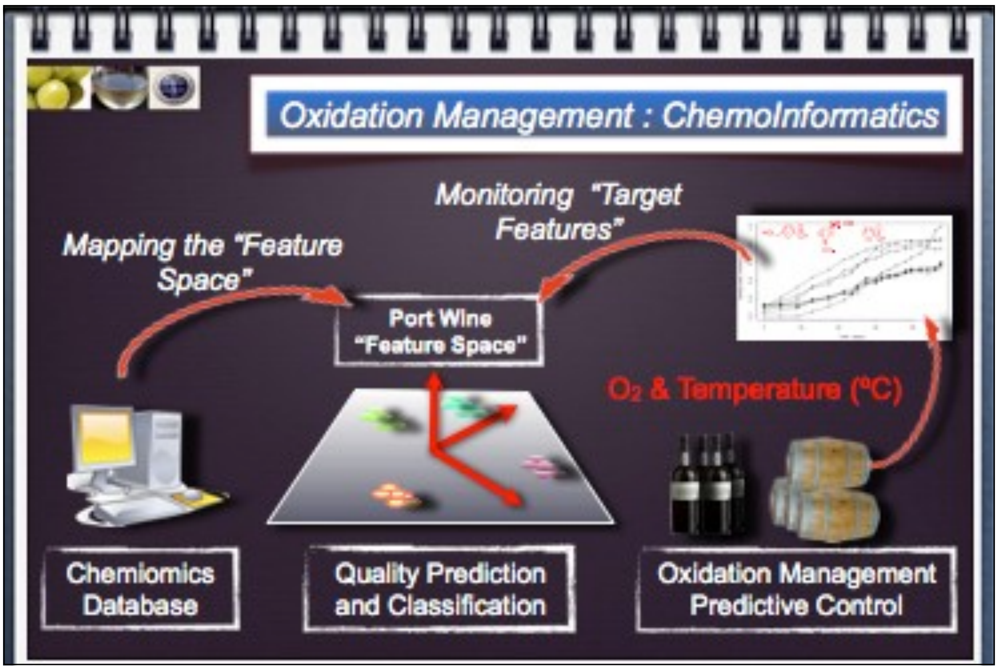

t = 10 years; T = 10 °C
Permeability : 1,5 (mg/L)/ 365 (days)
"Monte Carlo" : 50 % dispersion
Oxygen Daily Intake
Consumed Oxygen
Sotolon
Furfural
5MF
5HMF
cis-dioxane
cis-dioxolane
trans-dioxolane
Frequency

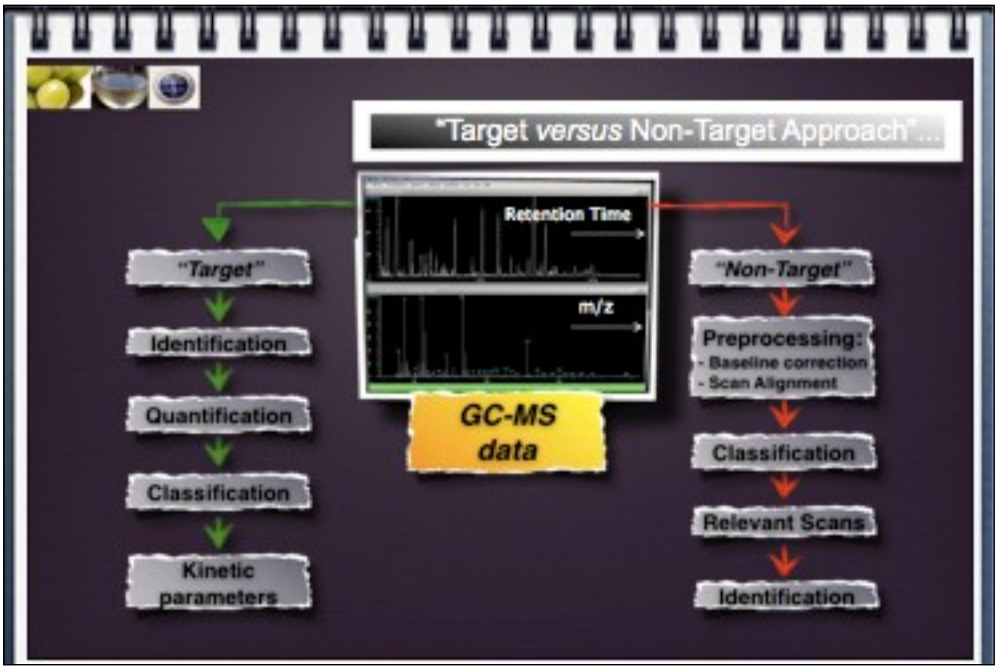

"Clustering" : 10 years "Vintage"
time = 10 years
T = 10 °C
Height
5 Years
10 Years
20 Years


"Clustering" : 10 years "Vintage"
time = 10 years
T = 20 °C
Height
5 Years
10 Years
20 Years

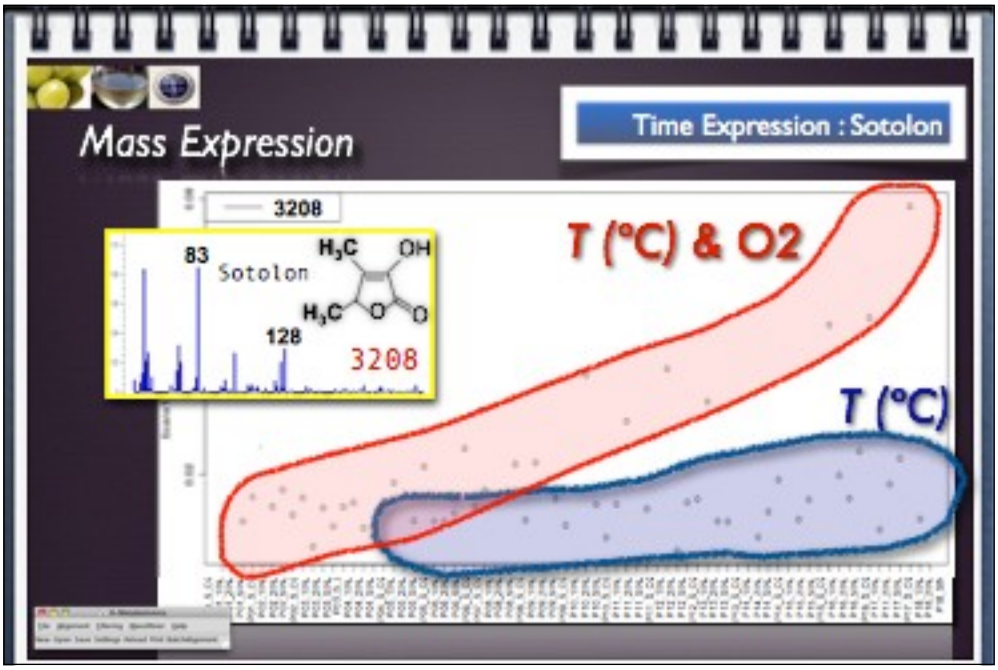

"Clustering" : 10 years "Tawny"
time = 10 years
T = 10 ºC
Height
5
Years
10+
Years
20
Years


"Clustering" : 10 years "Tawny"
time = 10 years
T = 20 ºC
Height
5
Years
10+
Years
20
Years

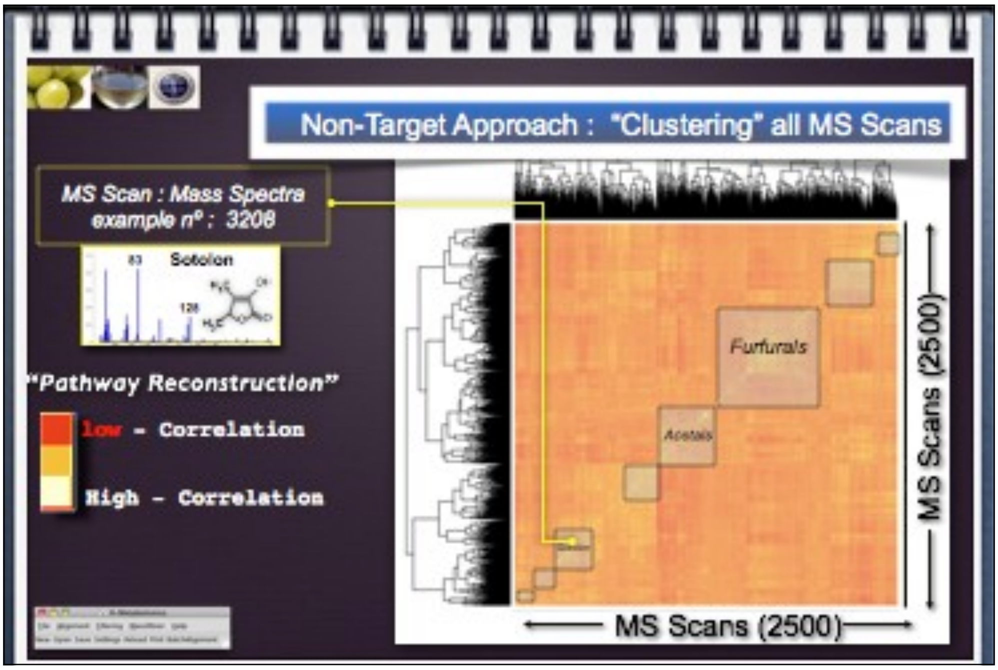

Oxidation Management : ChemoInformatics
Monitoring "Target Features"
Mapping the "Feature Space"
Port Wine "Feature Space"
O2 & Temperature (ºC)
Chemiomics Database
Quality Prediction and Classification
Oxidation Management Predictive Control



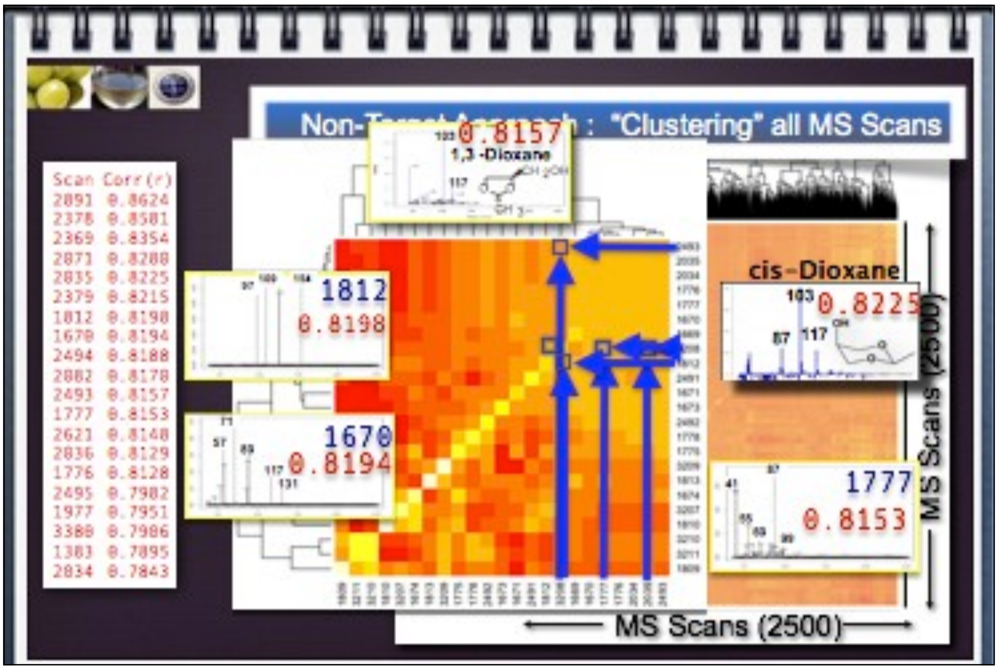
"Target versus Non-Target Approach"...
Retention Time
m/z
GC-MS data
"Target"
Identification
Quantification
Classification
Kinetic parameters
"Non-Target"
Preprocessing:
- Baseline correction
- Scan Alignment
Classification
Relevant Scans
Identification

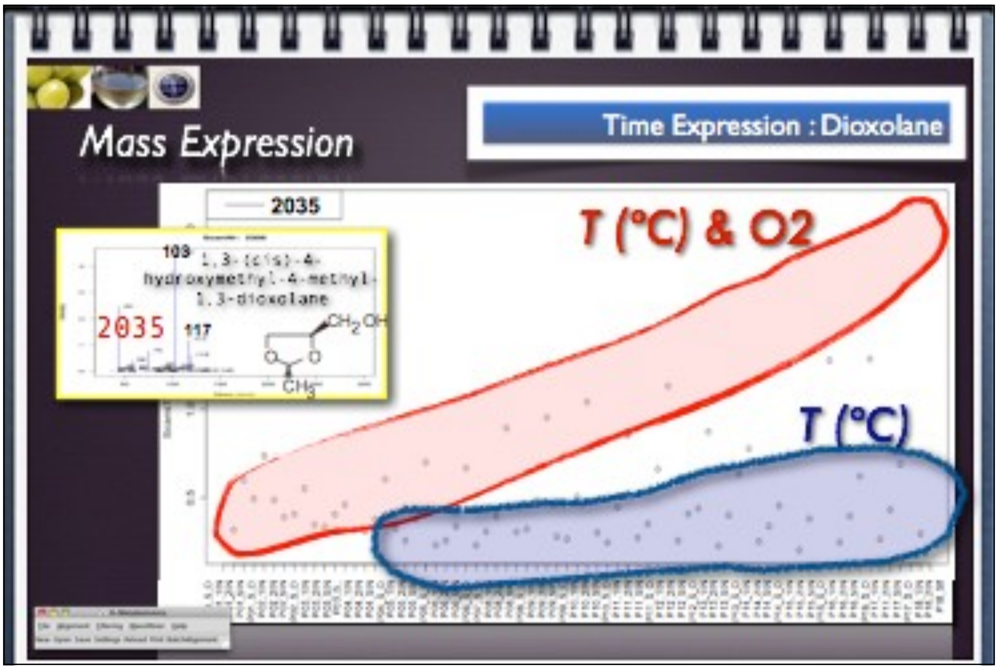


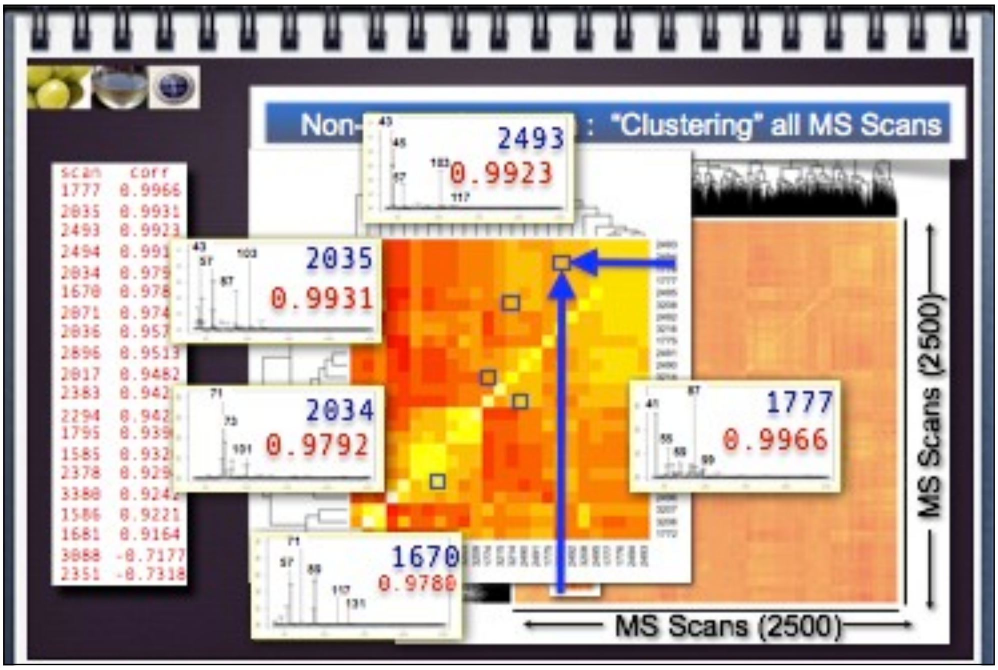
Mass Expression
Time Expression : Sotolon
3208
83
Sotolon
128
3208
T (°C) & O2
T (°C)

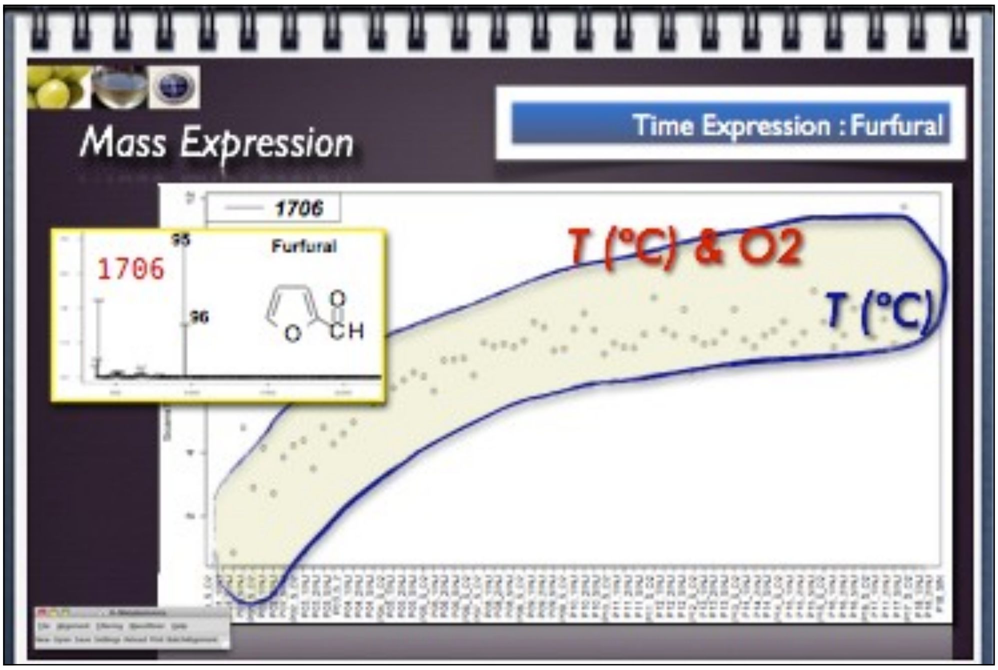


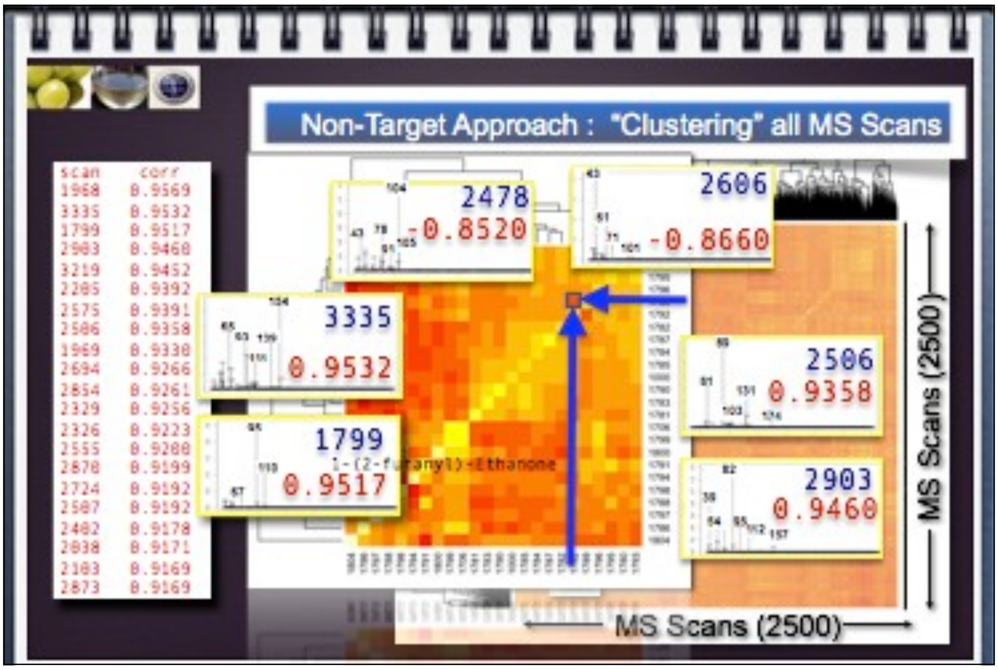
Non-Target Approach : "Clustering" all MS Scans
MS Scan : Mass Spectra example n° : 3208
83
Sotolon
128
"Pathway Reconstruction"
low - Correlation
High - Correlation
Furfurals
Acetals
MS Scans (2500)
MS Scans (2500)


Non-Target Approach : "Clustering" all MS Scans
0.8157
1,3-Dioxane
1812
0.8198
1670
0.8194
cis-Dioxane
0.8225
1777
0.8153
Scan Corr(r)
2891 0.8624
2378 0.8581
2369 0.8354
2871 0.8288
2835 0.8225
2379 0.8215
1812 0.8198
1670 0.8194
2494 0.8188
2882 0.8178
2493 0.8157
1777 0.8153
2621 0.8148
2836 0.8129
1776 0.8128
2495 0.7982
1977 0.7951
3388 0.7986
1383 0.7895
2834 0.7843
MS Scans (2500)
MS Scans (2500)


Mass Expression
Time Expression : Dioxolane
2035
1,3-(cis)-4-hydroxymethyl-4-methyl-1,3-dioxolane
2035
T (°C) & O2
T (°C)


Non-... : "Clustering" all MS Scans
2493
0.9923
2035
0.9931
2034
0.9792
1777
0.9966
1670
0.9780
scan corr
1777 0.9966
2035 0.9931
2493 0.9923
2494 0.991
2034 0.979
1670 0.978
2871 0.974
2836 0.957
2896 0.9513
2017 0.9482
2383 0.942
2294 0.942
1795 0.939
1585 0.932
2378 0.929
3380 0.924
1586 0.9221
1681 0.9164
3088 -0.7177
2351 -0.7318
MS Scans (2500)
MS Scans (2500)





Conclusions

In order to optimize "Sensory Quality" three conditions must be addressed :

1. "Brand Key" Oxygen dependence;

2. Kinetic studies are indispensables to establish temporal relationships between wine constituents and infer the chemical network of reactions - the "chemiomics".

3. Oxygen regimes of the container need to be provided.

Appling high-throughput data mining methodologies will allow the understanding of the complexity of wine aging : i) identifying the compounds; ii) their reaction network; iii) kinetics and thermodynamics.


PORT
SWISS
Thank you !!!