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Port Wine Oxidation Management: A ChemoInformatics Approach

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Objectives

Further understand the Oxygen and Temperature effects on the flavor chemical profile on wine aging, namely by

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

ii) 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

iii) Highlighting other correlated compounds through a non targeted approach to allow better understanding of mechanisms "interfaces";

" Key-Odorants"

Phenylacetaldehyde

Methional

Sotolon

White Wine

off - Flavor

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

Escudero, A.; Hernandez-Orte, P.; Cacho, J. E.; Ferreira, V. J.
Agric. Food Chem. **2000**, 48, 4268-4272.

Sotolon

Porto, Sherry
Madeira Wines

positive - Flavor

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

Background: Mechanisms …

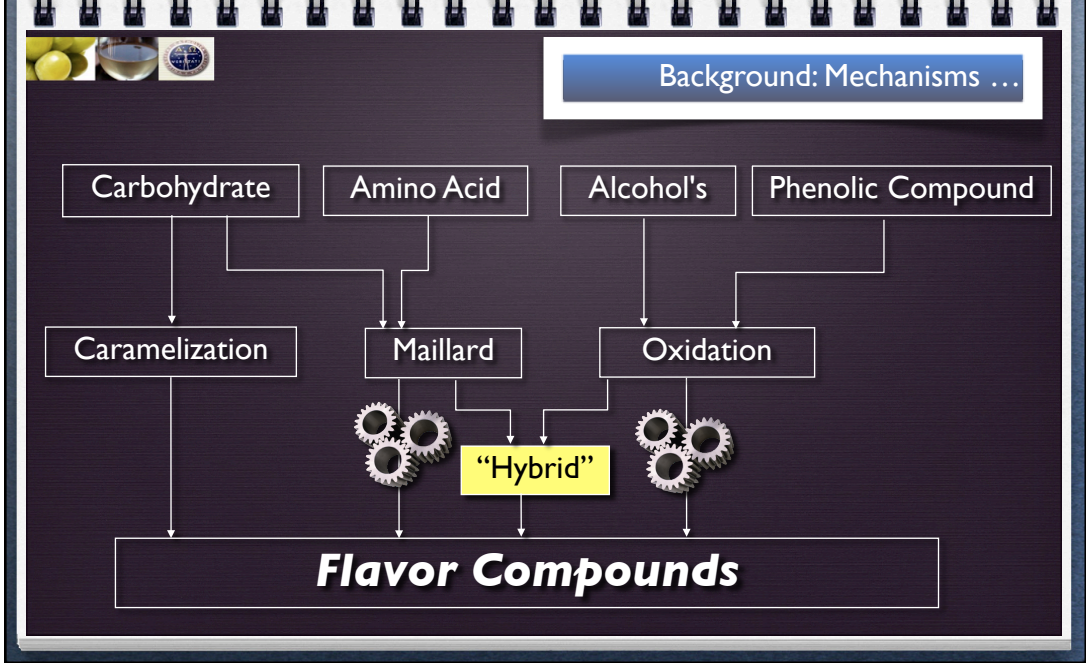
Major flavor impact compounds …

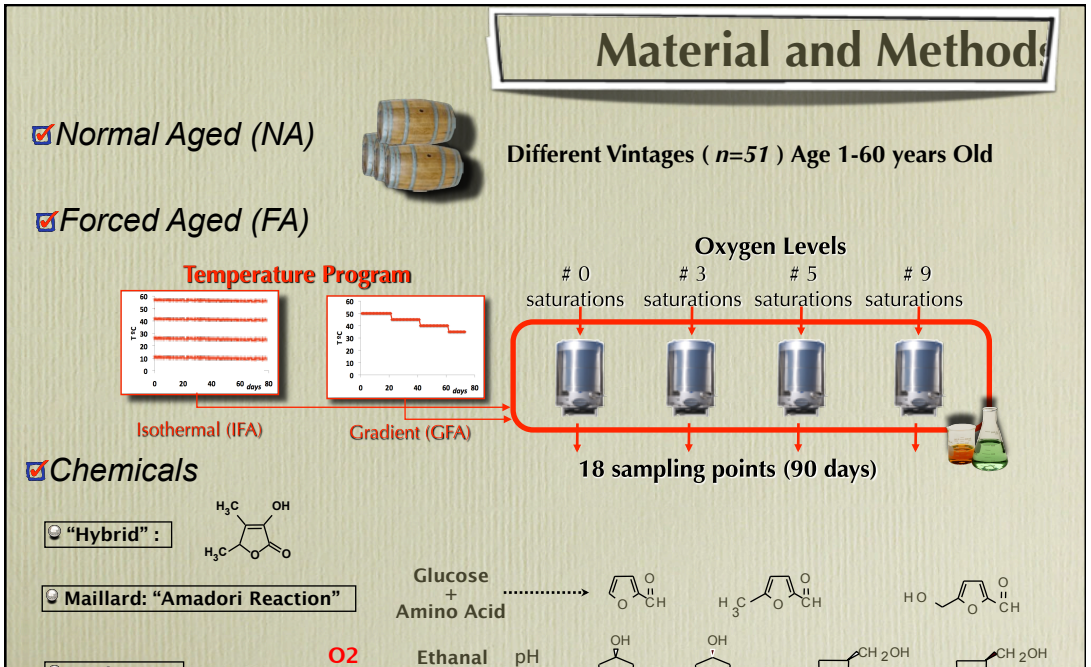
Rate of Formation Highly Dependent

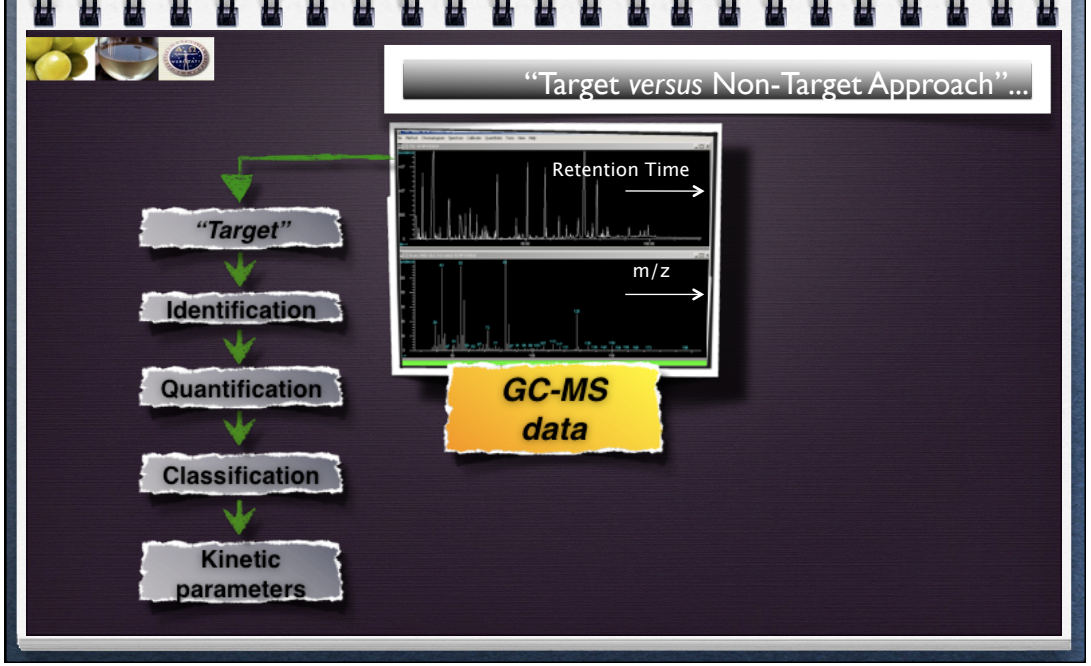
Oxygen Levels !!!

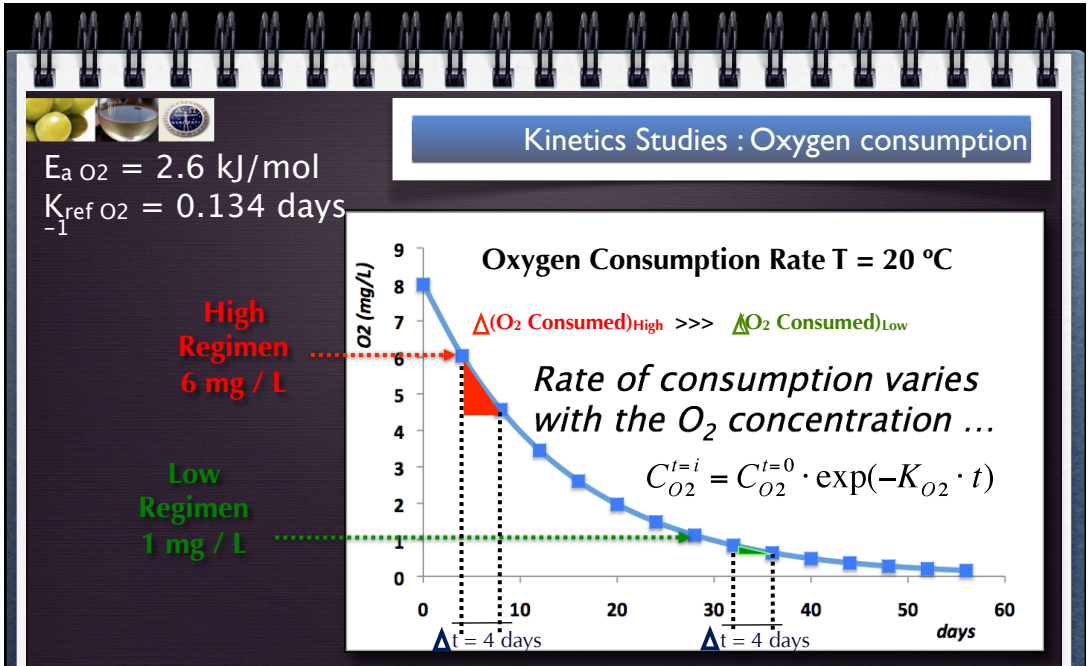
A C. Silva Ferreira, T. Hogg and P. Guedes de Pinho.
J. of Agric. Food Chem., 2003, 51 (5), 1373-1376.

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


Background: Mechanisms …
Carbohydrate
Amino Acid
Alcohol's
Phenolic Compound
Caramelization
Maillard
Oxidation
"Hybrid"
Flavor Compounds


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
O2
Ethanal
pH

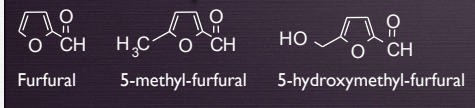

"Target versus Non-Target Approach"...
"Target"
Identification
Quantification
Classification
Kinetic parameters
Retention Time
m/z
GC-MS data


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

Kinetics Studies : Furfurals & Acetals

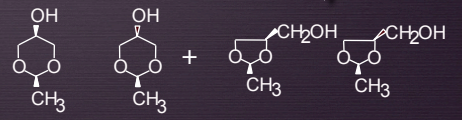
Maillard : Amadori Reaction

Glucose + Amino Acid



Oxidation

Ethanol $\xrightarrow{O2}$ Ethanal + Glycerol $\xrightarrow{pH}$



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

Ea; k – First Order reversible with Temperature

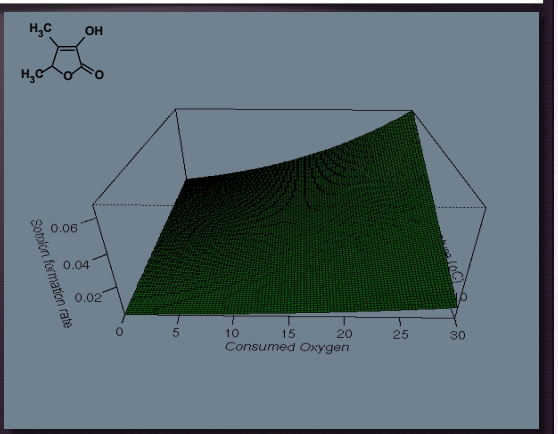
$E_{a\ furfural}$ = 143.1 kJ/mol
$K_{ref\ furfural}$ = 0.0009 days $^{-1}$

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

Kinetics Studies : Sotolon Rate of Formation

$$C_{Sot}^{t=i} = C_{Sot}^{t=0} + r_{Sot} \cdot t$$

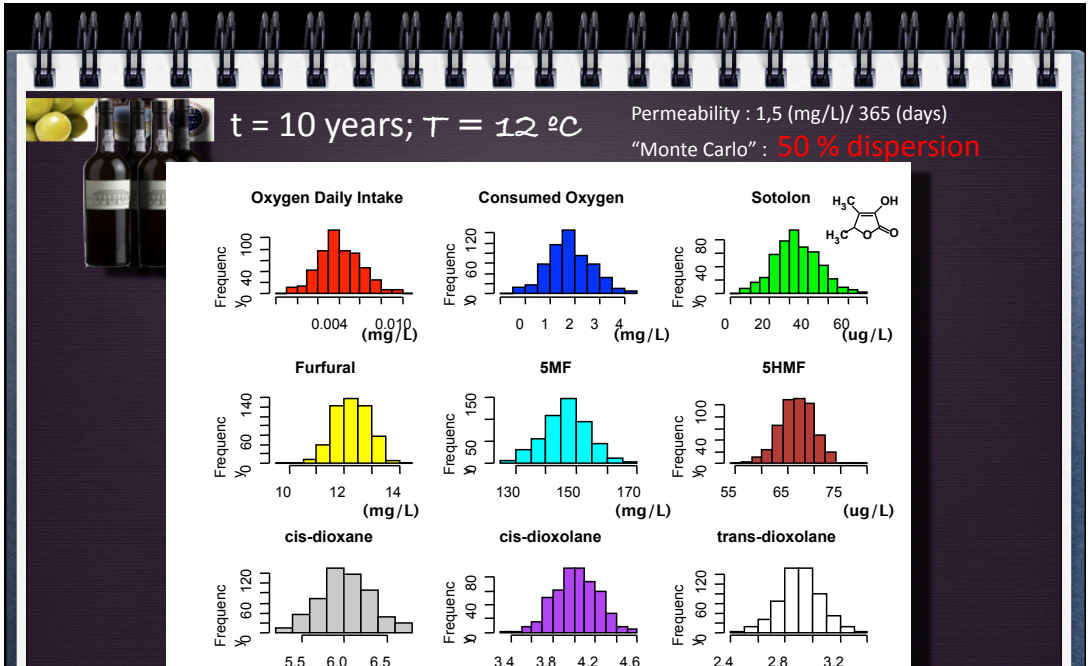
$$r_{Sot} = C_{O_2}^{Cons} \cdot k_{ref}^{Sot} \cdot \exp\left[\frac{E_a^{Sot}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$



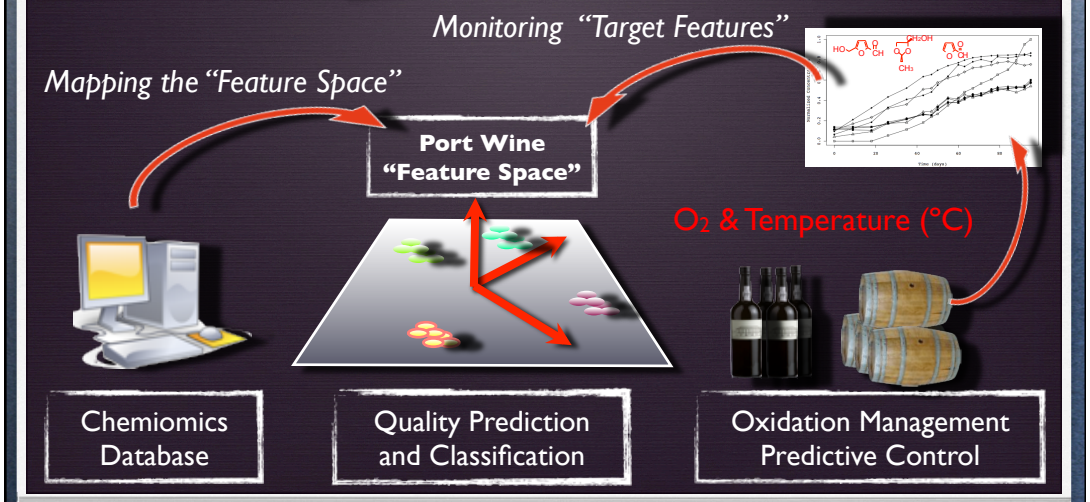
$E_{a\ sot}$ = 38 kJ/mol
$K_{ref\ sot}$ = 0.012 days $^{-1}$

Sotolon Rate of Formation
– directly proportional to oxygen consumption rate;

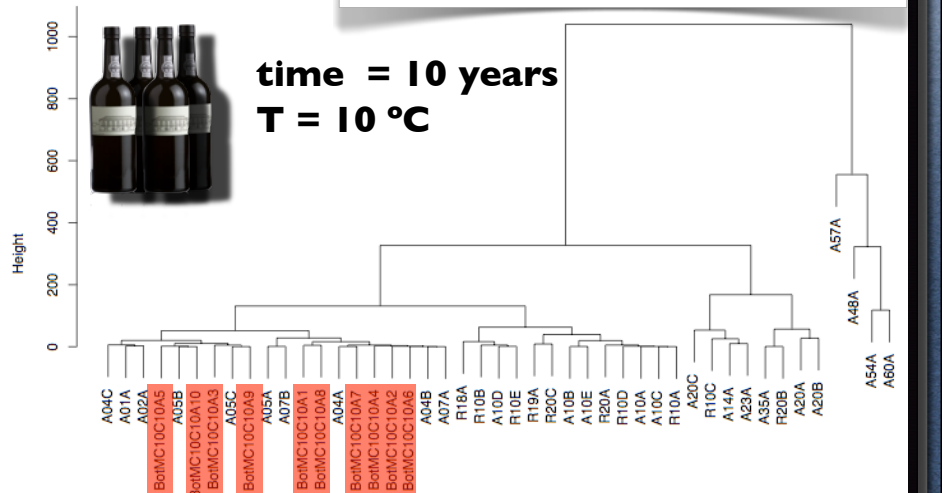

Permeability : 10 (mg/L)/ 365 (days)
"Monte Carlo" : 10 % dispersion
Monte Carlo
BONUS HOLE
PRICED RIGHT
OPTIONAL SEAT
ACCELERATOR
MORE
Oxygen D
(mg/L)
(ug/L)
-dioxolane
Jones & al. "004 AWRI REPORT WINE INDUSTRY JOURNAL, VOL 19 NO 3, MAY-JUNE 2004


t = 10 years; T = 12 ºC
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
(mg/L)
(ug/L)

Oxidation Management : ChemoInformatics



"Clustering" : 10 years "Vintage"

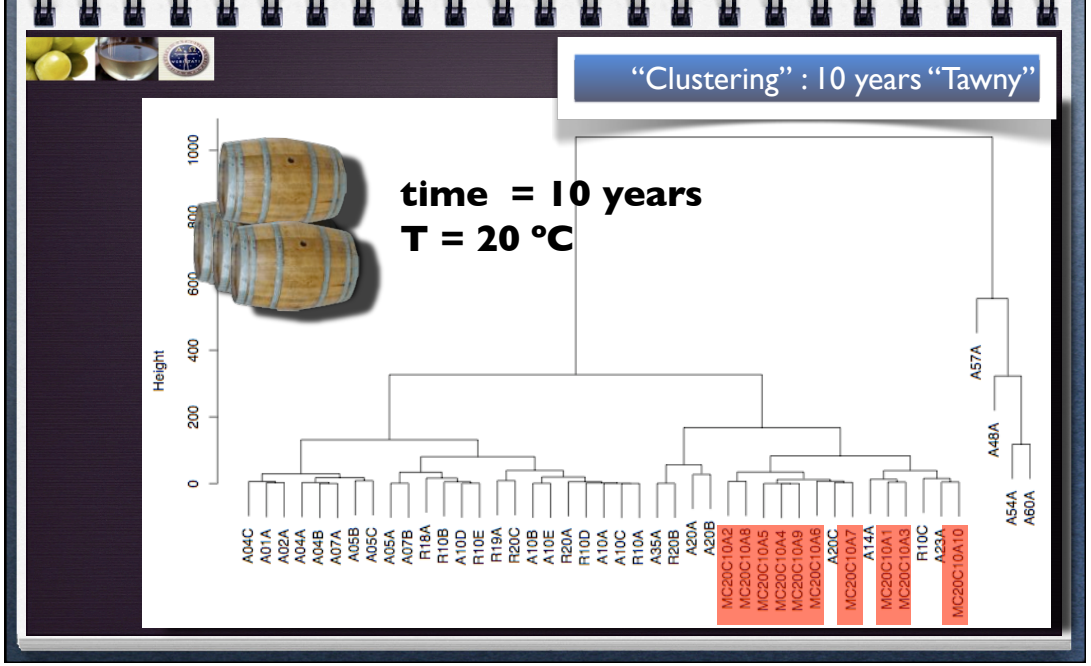


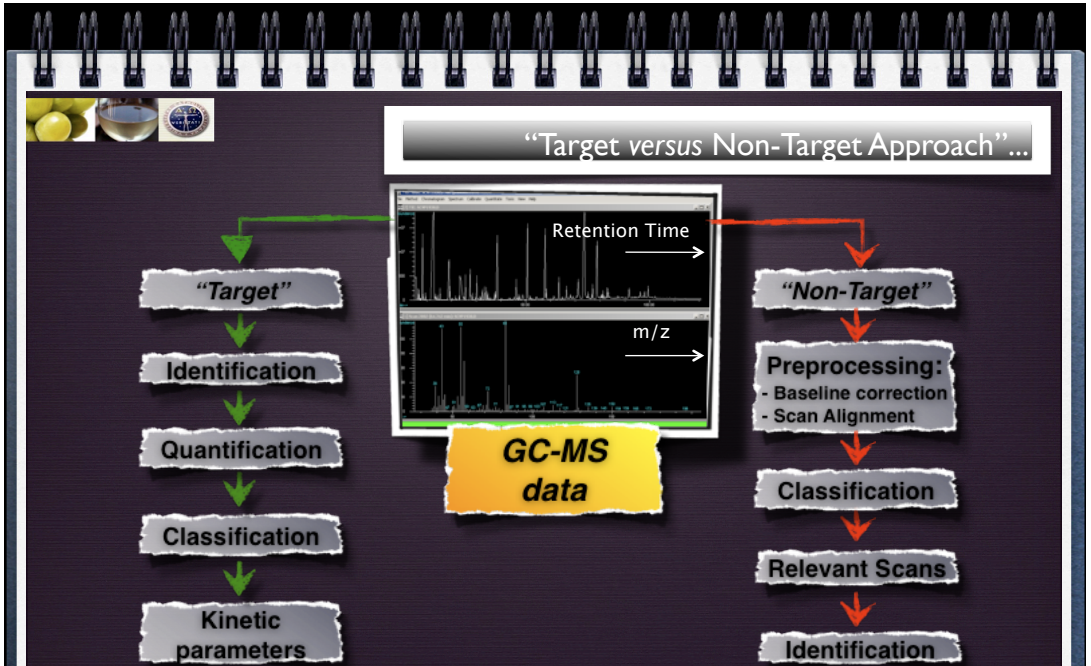
"Clustering" : 10 years "Vintage"

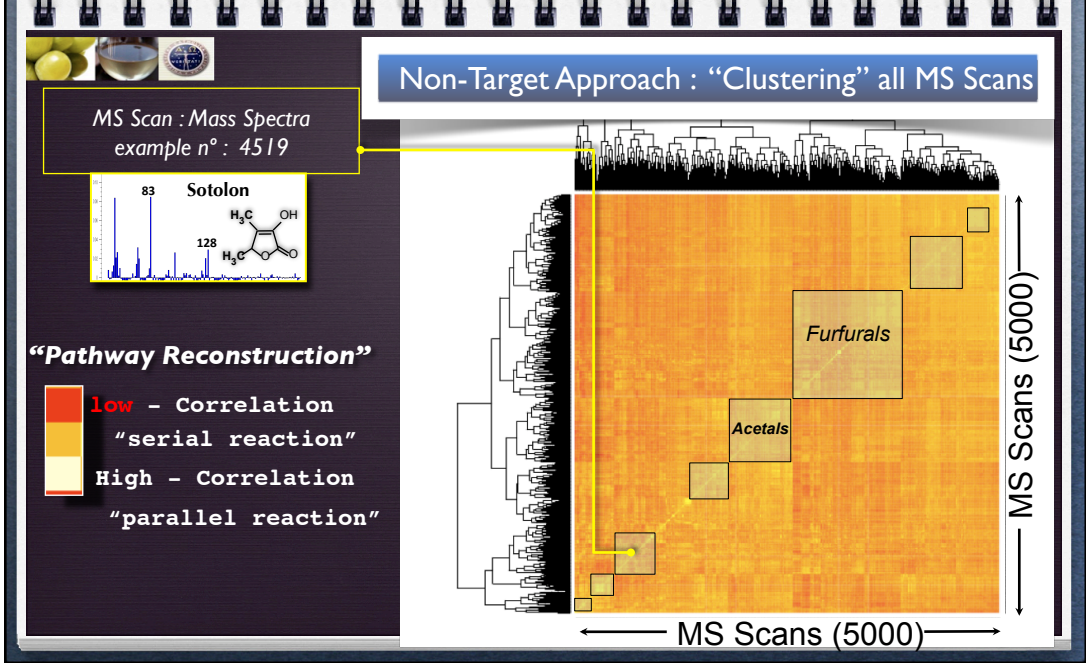
time = 10 years
T = 20 °C

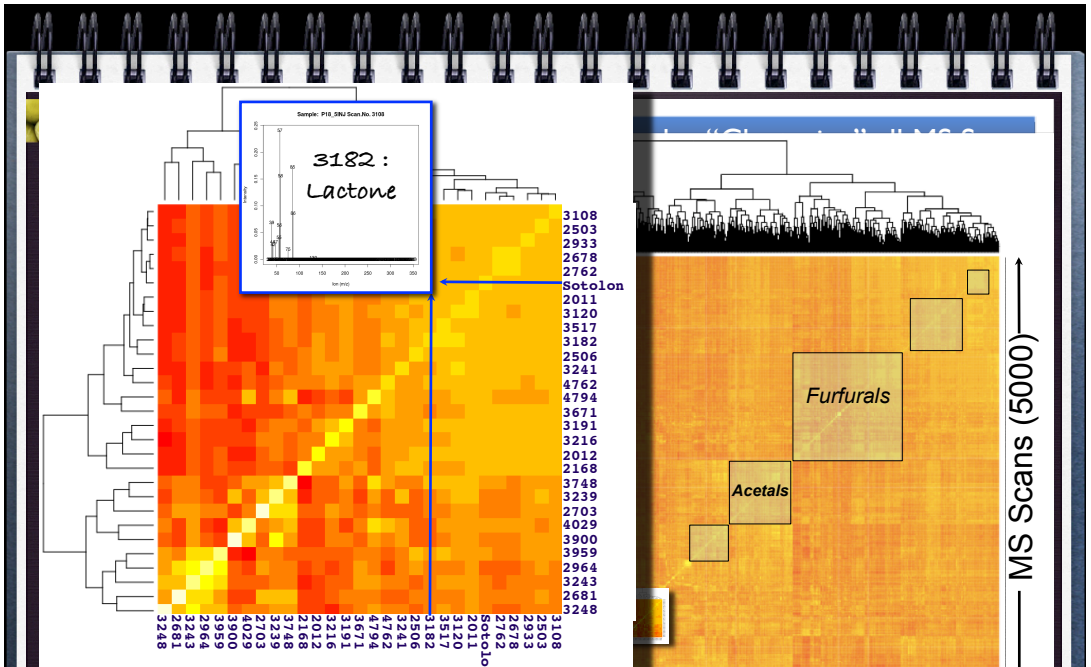
"Clustering" : 10 years "Tawny"

time = 10 years
T = 10 °C

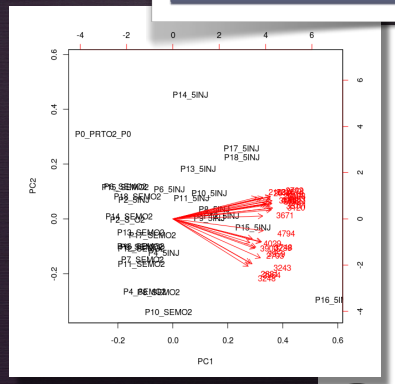

"Clustering" : 10 years "Tawny"
time = 10 years
T = 20 °C
Height
0
200
400
600
800
1000
A04C
A01A
A02A
A04A
A04B
A07A
A05B
A05C
A05A
A07B
R18A
R10B
A10D
R10E
R19A
R20C
A10B
A10E
R20A
R10D
A10A
A10C
R10A
A35A
R20B
A20A
A20B
MC20C10A2
MC20C10A8
MC20C10A5
MC20C10A4
MC20C10A9
MC20C10A6
A20C
MC20C10A7
A14A
MC20C10A1
MC20C10A3
R10C
A23A
MC20C10A10
A57A
A48A
A54A
A60A

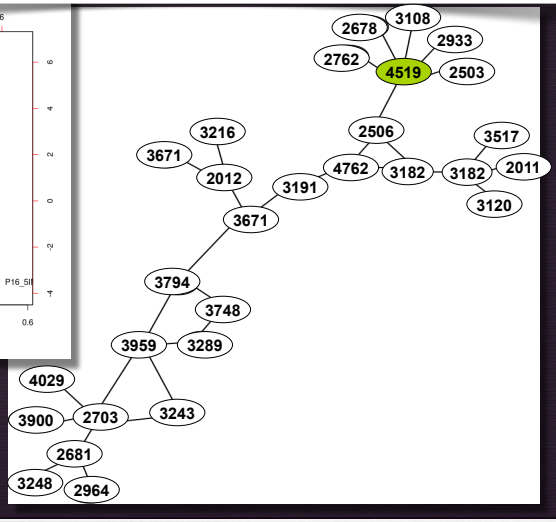

"Target versus Non-Target Approach"...
Retention Time
m/z
GC-MS data
"Target"
Identification
Quantification
Classification
Kinetic parameters
"Non-Target"
Preprocessing:
- Baseline correction
- Scan Alignment
Classification
Relevant Scans
Identification


Non-Target Approach : "Clustering" all MS Scans
MS Scan : Mass Spectra
example n° : 4519
83
Sotolon
128
"Pathway Reconstruction"
low - Correlation
"serial reaction"
High - Correlation
"parallel reaction"
Furfurals
Acetals
MS Scans (5000)
MS Scans (5000)


3182 :
Lactone
3108
2503
2933
2678
2762
Sotolon
2011
3120
3517
3182
2506
3241
4762
4794
3671
3191
3216
2012
2168
3748
3239
2703
4029
3900
3959
2964
3243
2681
3248
Furfurals
Acetals
MS Scans (5000)
MS Scans (5000)

Non-Target Approach : "Network Reconstruction"



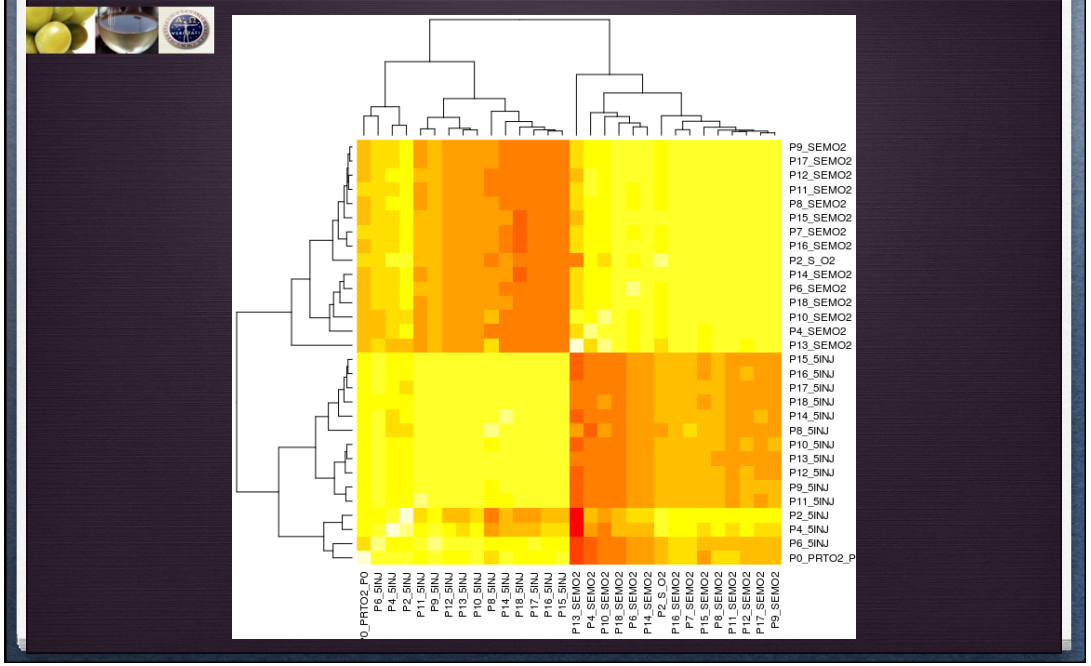


Conclusions

1. Oxygen Management and Temperature proved to be effective tools in order to attain a desired chemical "quality-profile" in Port wine,

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

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


P9_SEMO2
P17_SEMO2
P12_SEMO2
P11_SEMO2
P8_SEMO2
P15_SEMO2
P7_SEMO2
P16_SEMO2
P2_S_O2
P14_SEMO2
P6_SEMO2
P18_SEMO2
P10_SEMO2
P4_SEMO2
P13_SEMO2
P15_5INJ
P16_5INJ
P17_5INJ
P18_5INJ
P14_5INJ
P8_5INJ
P10_5INJ
P13_5INJ
P12_5INJ
P9_5INJ
P11_5INJ
P2_5INJ
P4_5INJ
P6_5INJ
P0_PRTO2_P
P0_PRTO2_P0
P8_5INJ
P4_5INJ
P2_5INJ
P11_5INJ
P9_5INJ
P12_5INJ
P13_5INJ
P10_5INJ
P6_5INJ
P14_5INJ
P18_5INJ
P17_5INJ
P16_5INJ
P15_5INJ
P13_SEMO2
P4_SEMO2
P10_SEMO2
P18_SEMO2
P6_SEMO2
P14_SEMO2
P2_S_O2
P16_SEMO2
P7_SEMO2
P15_SEMO2
P8_SEMO2
P11_SEMO2
P12_SEMO2
P17_SEMO2
P9_SEMO2