

# Managing Wine Quality : Strategies and Tools

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Portugal - Vila Real

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## Quality

### *Comply with the requirements*

*Organoleptic properties and Sensory : composition, stability*

*Product Performance : flavor technology, fitness for use*

*Regulatory compliance : authenticity, labeling, chemical identity, purity*

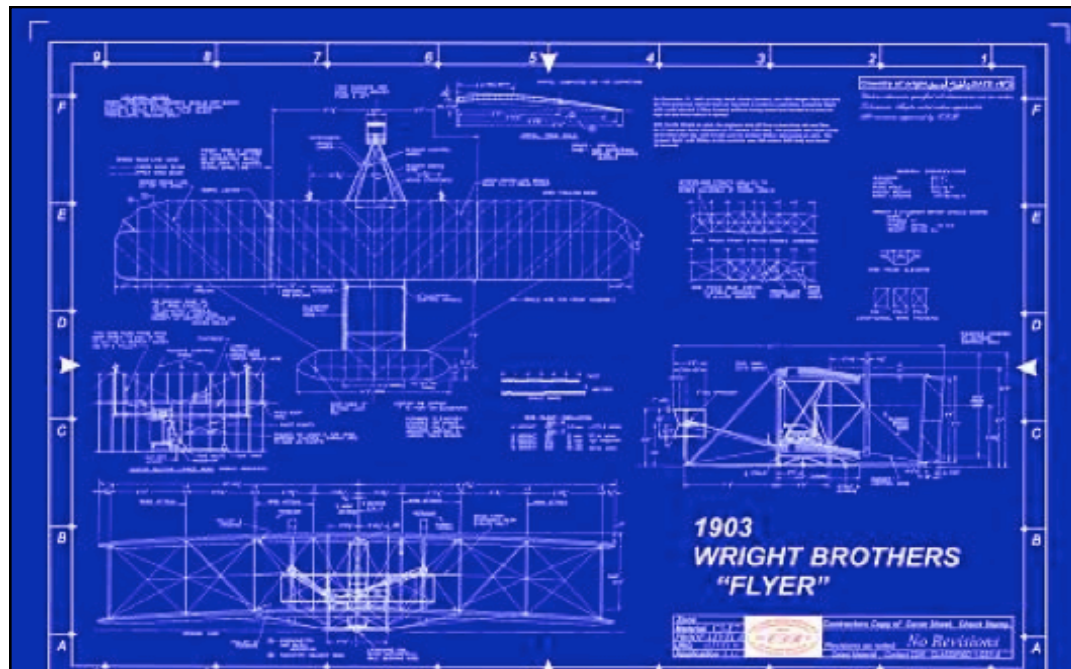
*Food ethical compliance : kosher, halal, organic*

### *Absence of faults*

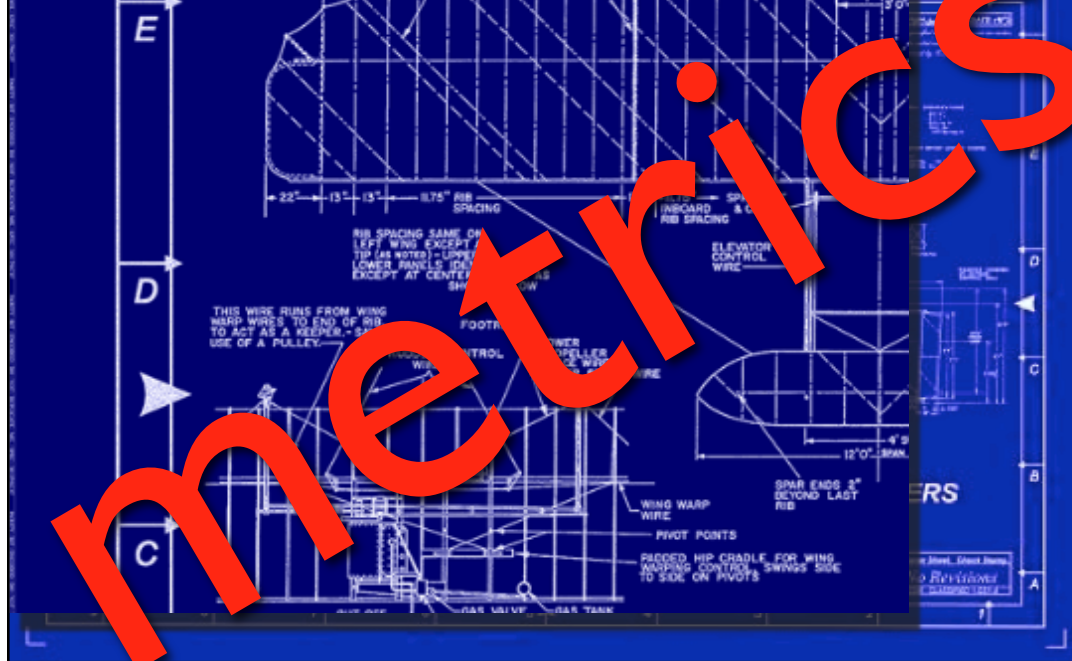
*Free from off-flavors*



# Wine Composition: the Big Picture




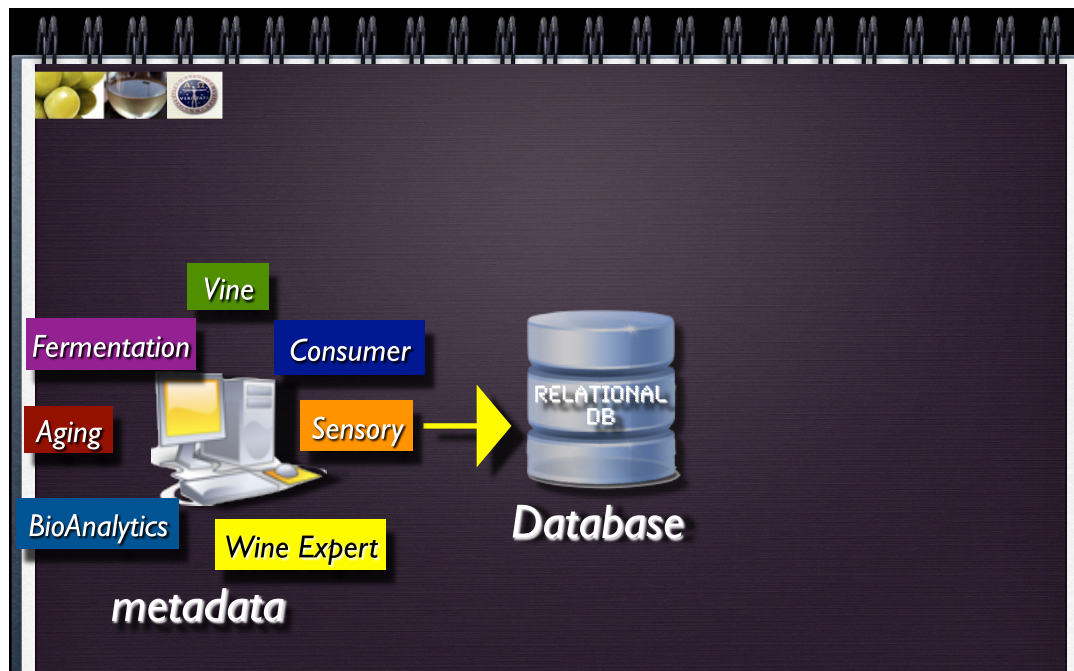




Why do "metrics" matters ??

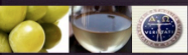
- Authenticity
- Quality







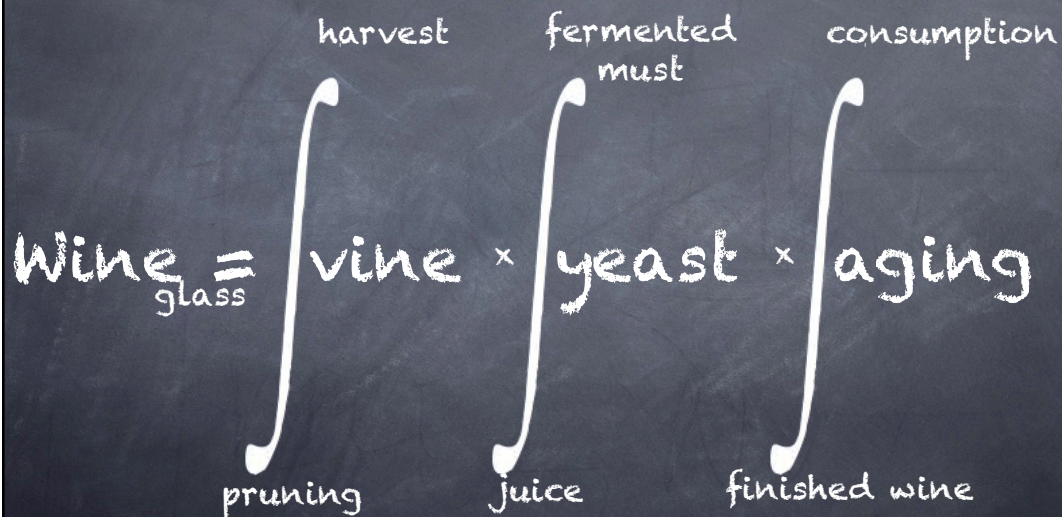




# Strategies



## Complexity





NMR

mg/L

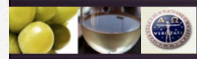
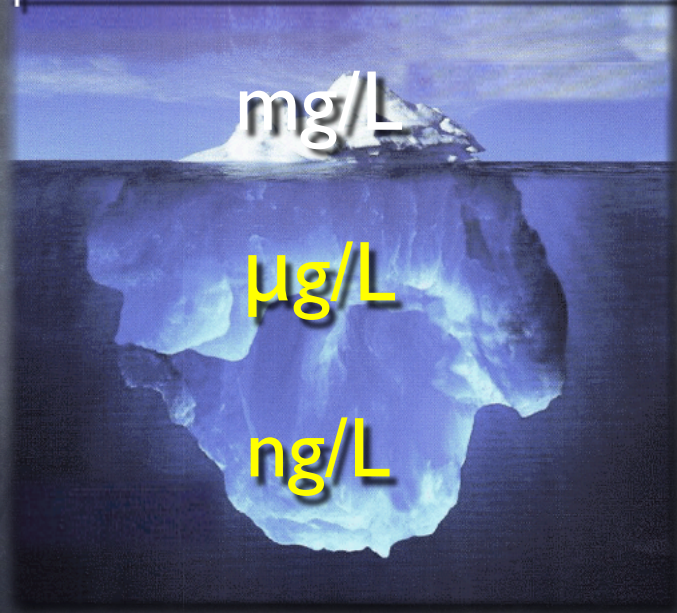
MS

$\mu\text{g/L}$

Others

ECD...

ng/L



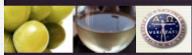
“Workflow”

1. Extract Sensory Information

2. Key-Molecules Identification

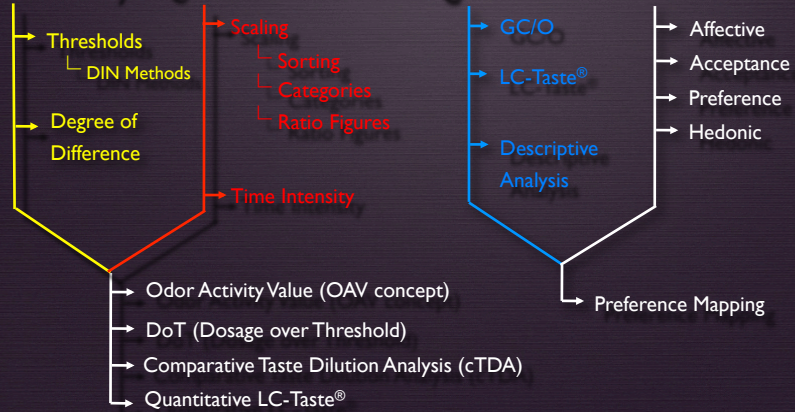
3. Mechanisms of Formation

4. Kinetic Measurements



# Compliance to Sensory Specifications

## Sensitivity Quantitative Qualitative Consumer Tests



Krammer, G. et al. 2008, 12thVveurman Flavour Research Symposium, 1-4 July 2008, Interlaken, Switzerland.

This collage illustrates sensory analysis in practice. On the left, a radar chart displays the mean values for two products: Touriga Nacional (red line) and Tinta Roriz (green line). The chart has eight axes representing different sensory attributes: Citrus, Balsamic, Vegetal, Dry fruit, Spicy, Berry fruits, Tree fruits, and Tropical Fruits. The Touriga Nacional profile is characterized by high values in Citrus, Balsamic, and Dry fruit, while Tinta Roriz shows higher values in Vegetal and Berry fruits. Below the chart is a table for 'Means = GLM procedure' with columns for 'Attribute' and 'Mean'. On the right, a photograph shows a sensory panel of people seated around a table, evaluating samples. Labels for 'Touriga Nacional' and 'Tinta Roriz' are overlaid on the photo. Other labels include 'Herbaceous', 'Bergamot', and 'Floral'. The background of the collage shows various sensory analysis tools and samples.





# “Workflow”

1. Extract Sensory Information

2. Key-Molecules Identification



*Which Compounds Should be  
Quantified ?????*



# "Correlate Sensory & Chemical Data"



Sensory Analysis

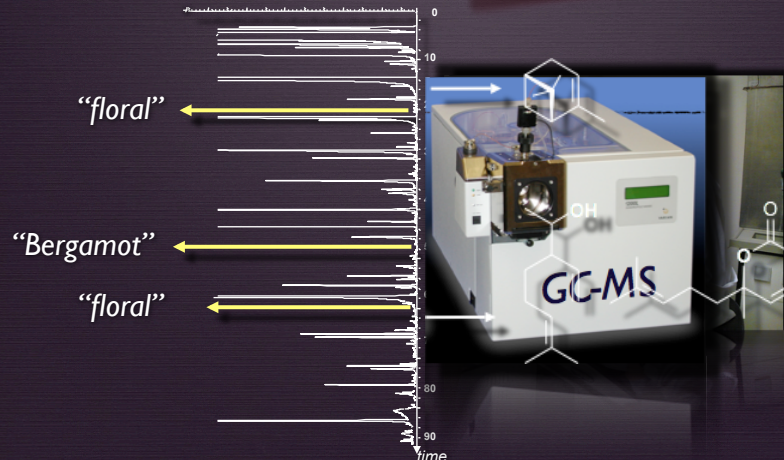


Instrumental Analysis

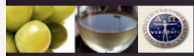
*Hybrid techniques*



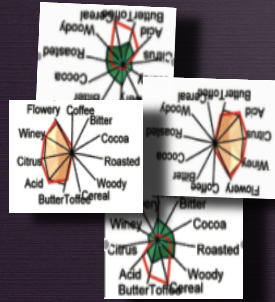
# Hybrid Techniques



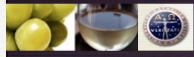
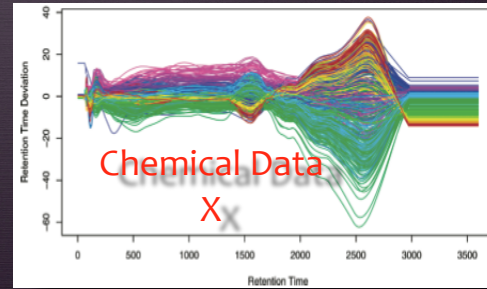




in-Silico ...



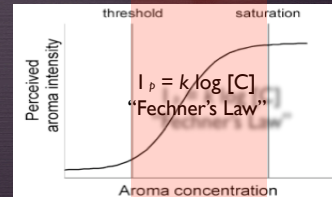
Sensory Data  
Y



in-Silico...

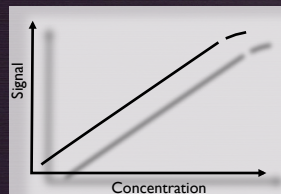
# Sensory

- Sensory profile : "Brain construction" relations between attributes
- Psychophysics : Intensity of Stimulus is a sigmoid curve



# Chemical

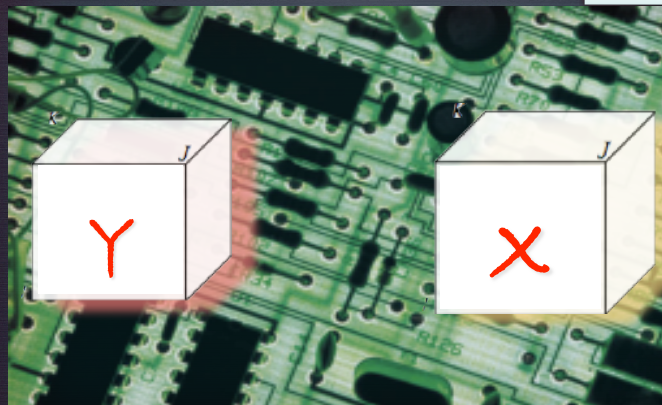
- Independent of compound variations ...
- Detector has (usually) a linear behavior





Data Fusion : Different metrics ...

in-Silico ...



Christian Lindinger,\* David Labbe, Philippe Polle, Andreas Rytz, M. Juillerat, C. Yeretjian and I. Blank. Machine Tastes Coffee: Instrumental Approach To Predict the Sensory Profile of Espresso Coffee. *Anal. Chem.*, 2008, 1574-1581.



“Workflow”

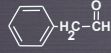
1. Extract Sensory Information
2. Key-Molecules Identification
3. Mechanisms of Formation



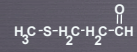


“Key-Odorants”

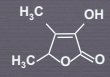
Phenylacetaldehyde



Methional



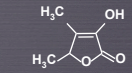
Sotolon



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

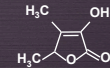
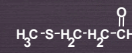
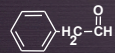
positive - Flavor

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 ...

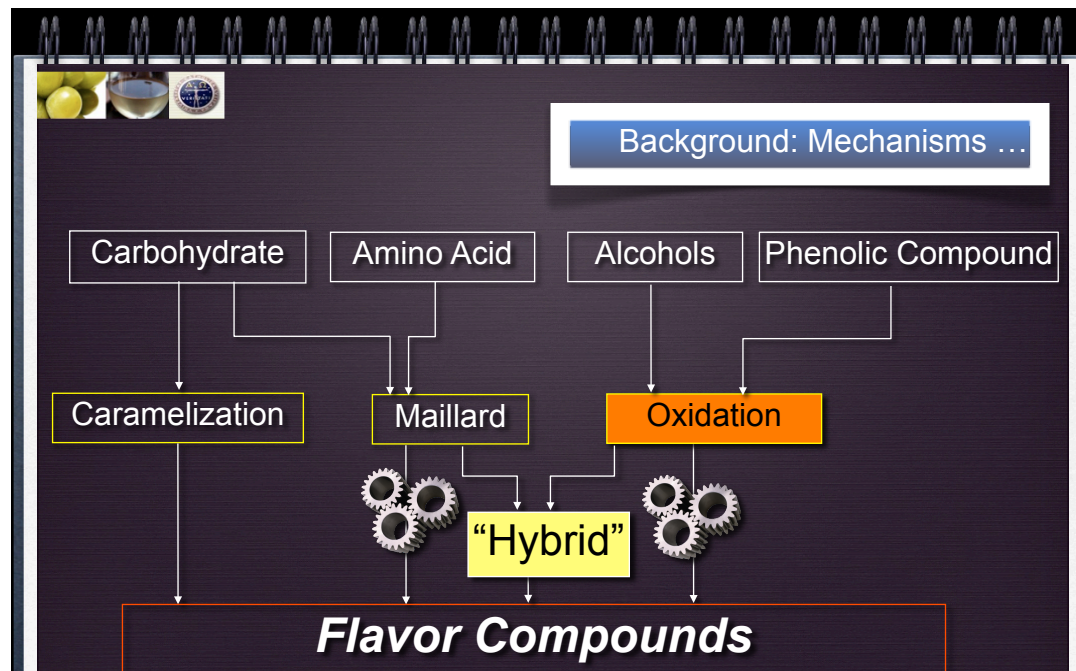
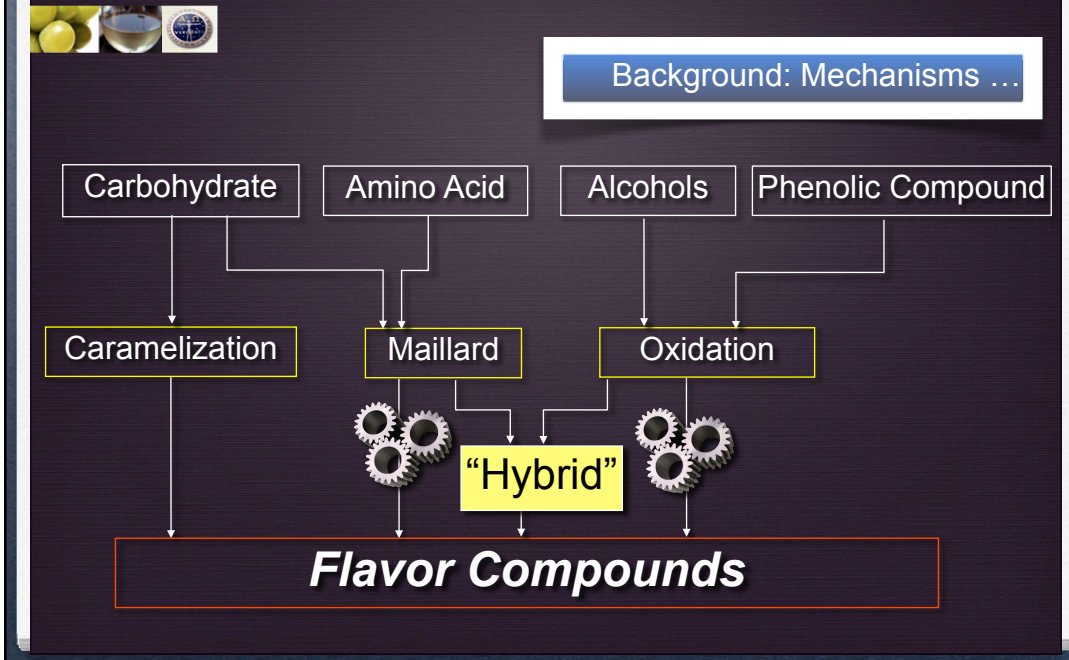


Rate of Formation Highly Dependent

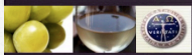
Oxygen Levels !!!

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

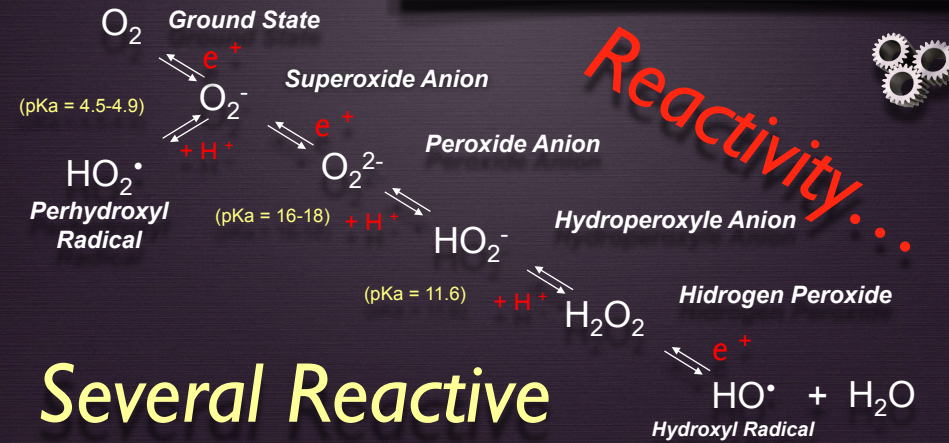
A.C. Silva Ferreira, Barbe J.C. and Bertrand A.B. *J. of Agric. Food Chem.* 2003, 51 (5), 1373-1376.





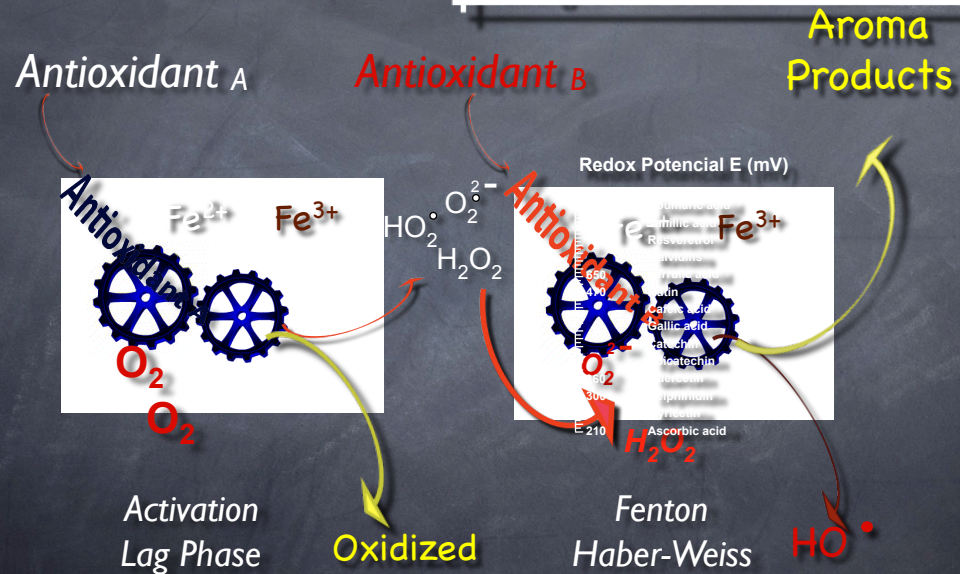


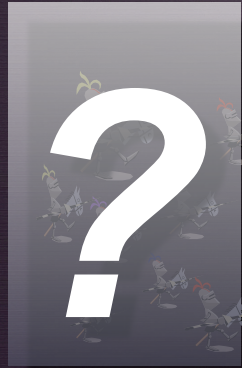
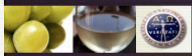
### Background: Oxygen Chemistry ...



## Several Reactive Oxygen Species ...

### Background: Oxidation Mechanism ...





***Antioxidants***



***Dissolved***



## **“Workflow”**

1. Extract Sensory Information

2. Key-Molecules Identification

3. Mechanisms of Formation

4. Kinetic Measurements



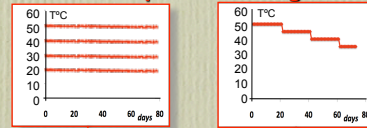
☑ Normal Aged (NA)



Different Vintages ( n=51 ) Age 1-60 years Old

☑ Forced Aged (FA)

**Temperature Program**

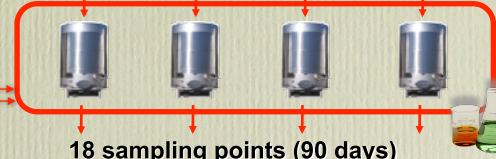


Isothermal (IFA)

Gradient (GFA)

**Oxygen Levels**

# 0 # 3 # 5 # 9  
saturations saturations saturations saturations



18 sampling points (90 days)

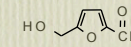
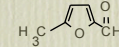
☑ Chemicals

☑ "Hybrid" :



☑ Maillard: "Amadori Reaction"

Glucose + Amino Acid



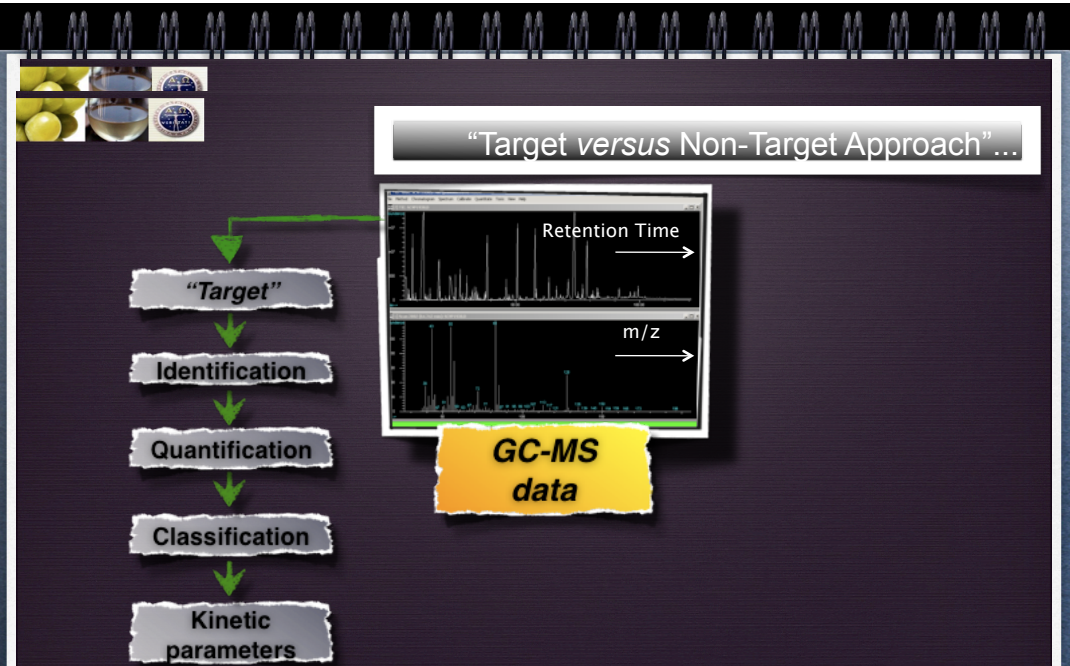
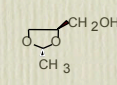
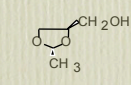
☑ Oxidation

Ethanol

O<sub>2</sub>

Ethanal + Glycerol

pH





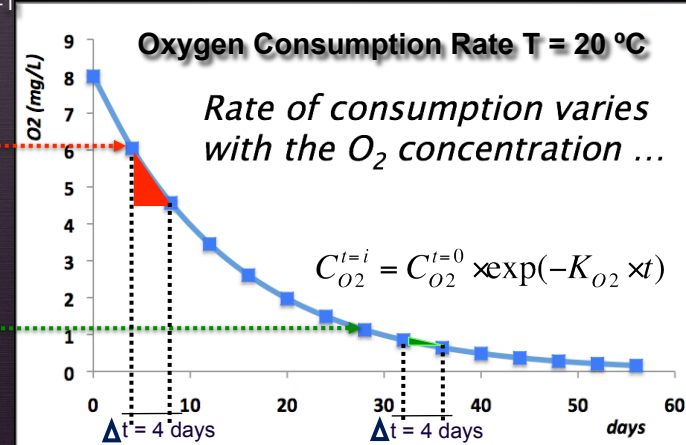
## Kinetics Studies : Oxygen consumption

$$E_{a O_2} = 2.6 \text{ kJ/mol}$$

$$K_{ref O_2} = 0.134 \text{ days}^{-1}$$

High Regimen  
6 mg / L

Low Regimen  
1 mg / L



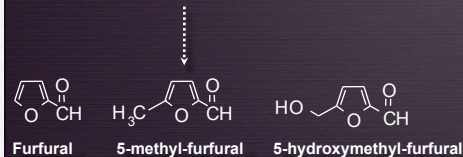
Oxygen - First Order with Temperature



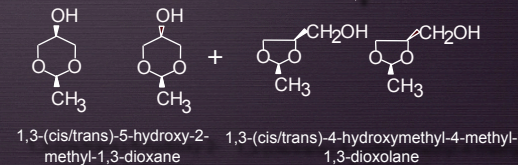
## Kinetics Studies : Furfurals & Acetals

### Maillard : Amadori Reaction

Glucose + Amino Acid



### Oxidation



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

E<sub>a</sub>; k - First Order reversible with Temperature

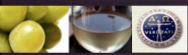
$$E_{a \text{ furfural}} = 143.1 \text{ kJ/mol}$$

$$K_{ref} = 0.0009 \text{ days}^{-1}$$

$$E_{a \text{ dioxane}} = 32.5 \text{ kJ/mol}$$

$$K_{ref} = 0.0011 \text{ days}^{-1}$$





## Kinetics Studies : Sotolon Rate of Formation

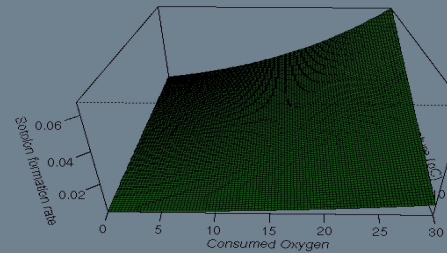
$$C_{Sot}^{t=i} = C_{Sot}^{t=0} + r_{Sot} \times t$$

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

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

### Sotolon Rate of Formation

- directly proportional to oxygen consumption rate;
- exponential dependent on storage temperature.



$t = 10 \text{ years}; T = 10 \text{ }^\circ\text{C}$

Permeability : 10 (mg/L)/ 365 (days)

"Monte Carlo" : 10 % dispersion

Oxygen Daily Intake

Consumed Oxygen

Sotolon

#### Step One: Implement Stochastic Kinetic Laws

Require: Initial Conditions: Concentrations, Temperature, Storage Time

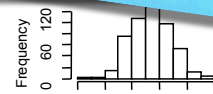
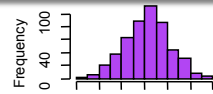
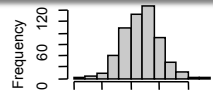
Require: Model Parameters: Kinetic Constants, Model Error, O<sub>2</sub> Daily Intake

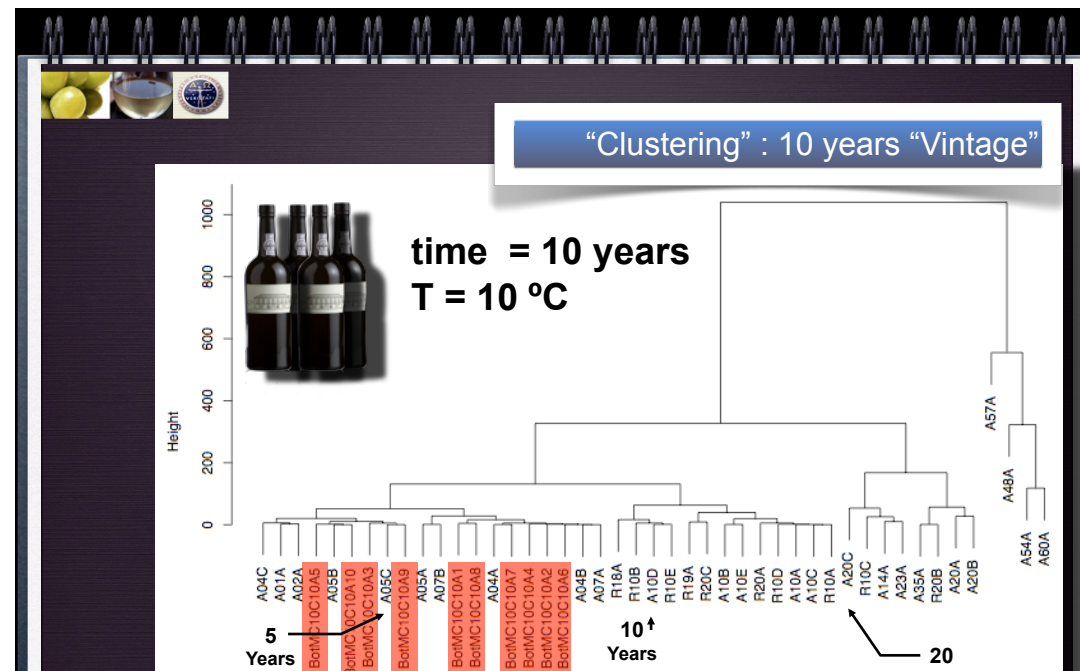
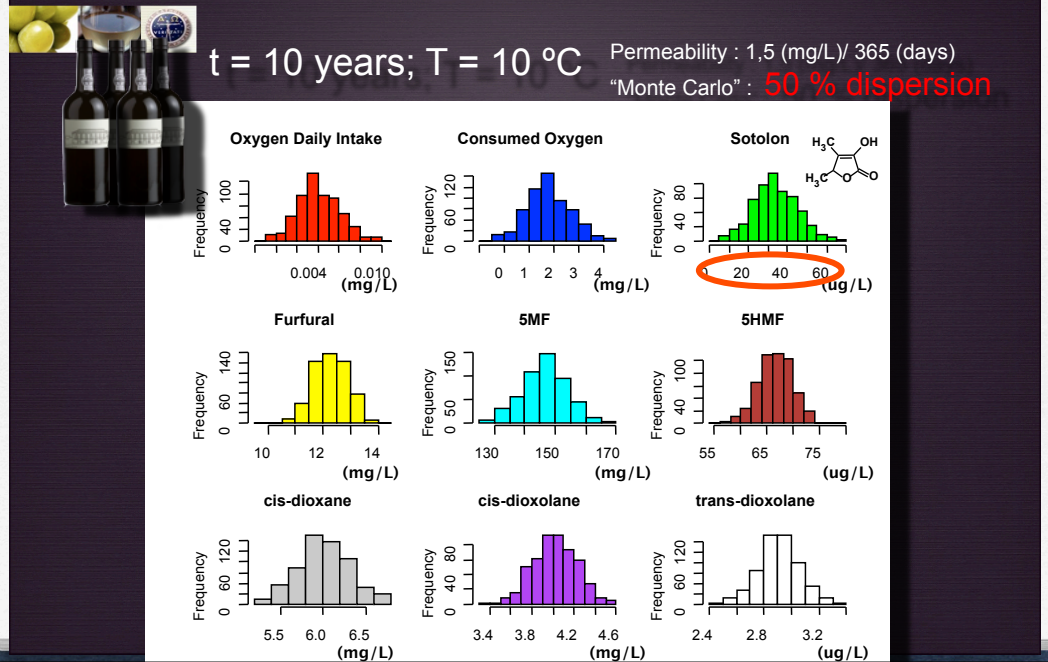
Require: Uncertainty in C<sub>0</sub>, C<sub>eq</sub>, k<sub>ref</sub> and E<sub>a</sub>

Ensure: Monte Carlo Statistical Significance: Number of Cases

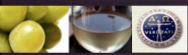
```

for i = 1 to NumberOfCases do
  for j = 1 to StorageTime.Increment=TimeStep do
    CO2[j] ← DetermineO2(j, Temperature, Error);
    ConsumedO2 ← CO20 - CO2[j];
    CSotolon ← CalculateSotolon(j, CSotolon0, ConsumedO2);
    QualityParameters ← Calculate1stOrderRev(j, InitialConc, Temperature, Error);
  end for
  MonteCarlo[j] ← AppendResult(O2, ConsumedO2, Sotolon, QualityParameters);
end for
Return MonteCarlo
  
```

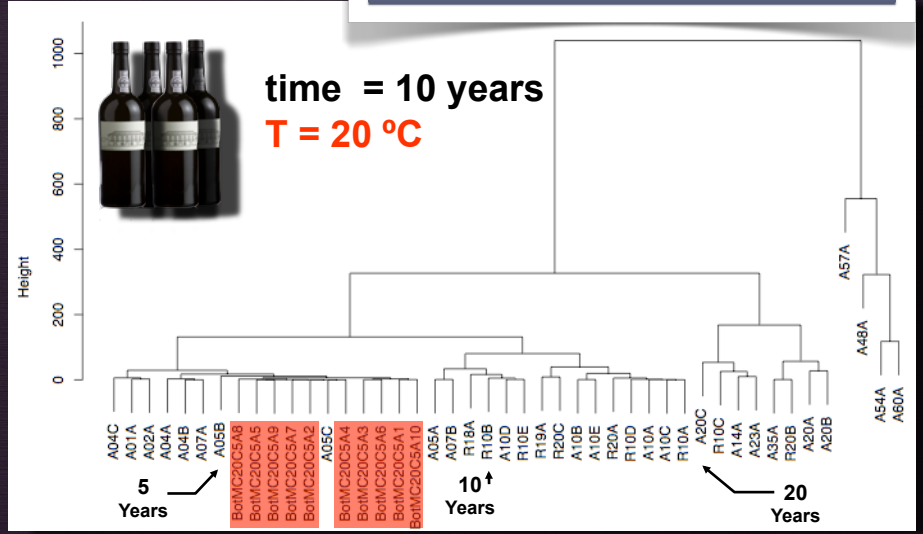




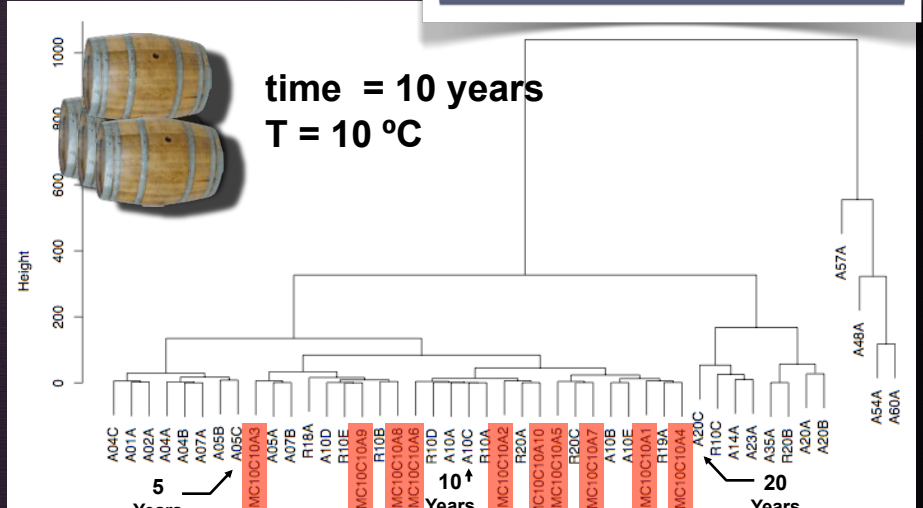


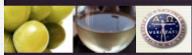


# "Clustering" : 10 years "Vintage"

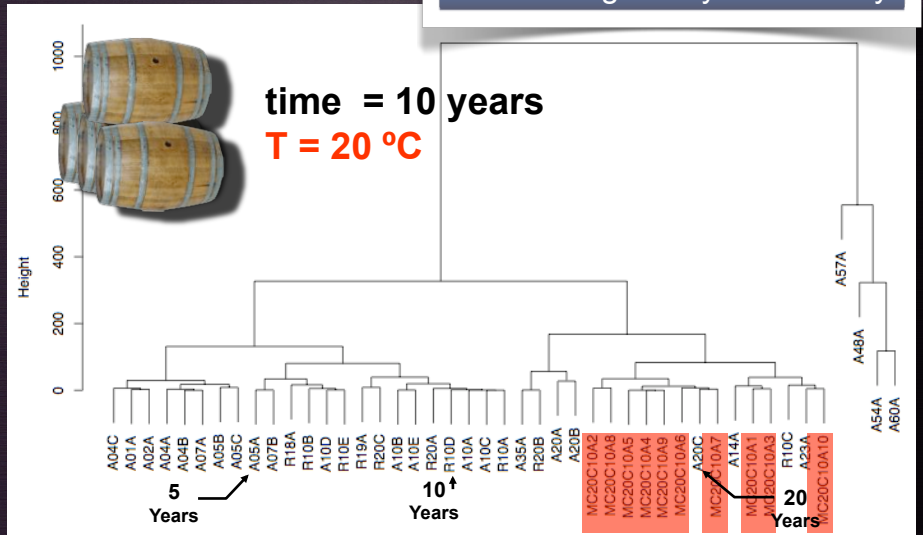


# "Clustering" : 10 years "Tawny"

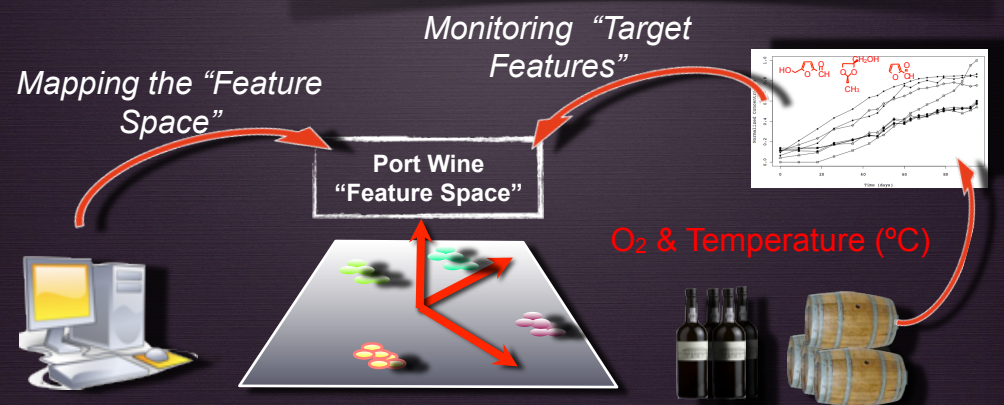




# “Clustering” : 10 years “Tawny”



# Oxidation Management : ChemInformatics

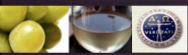


Cheminformatics Database

Quality Prediction and Classification

Oxidation Management Predictive Control

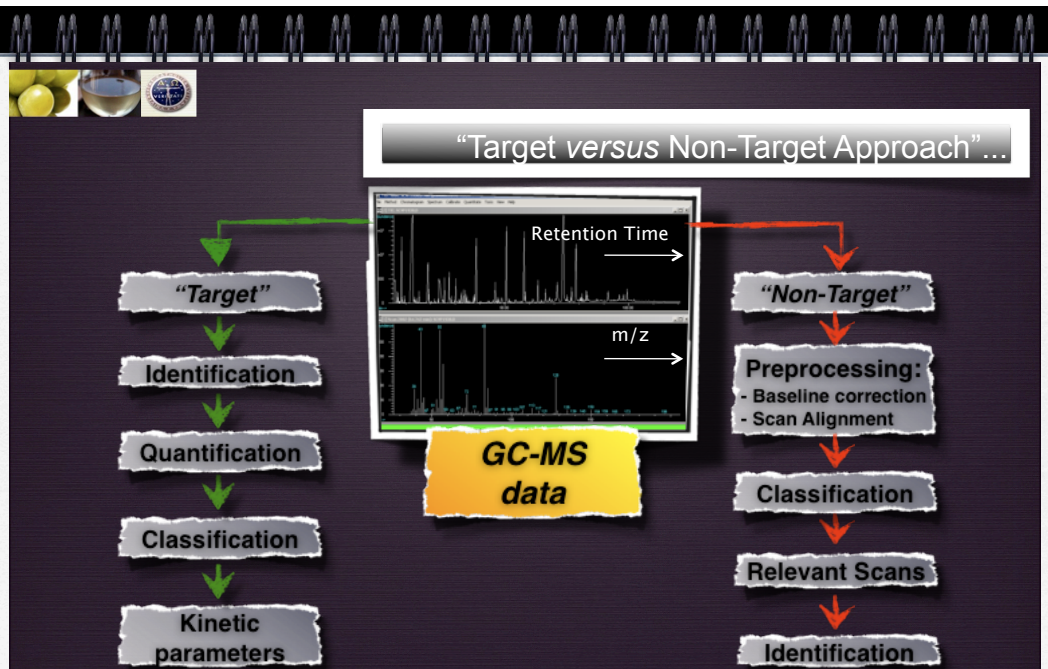


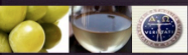


# Tools



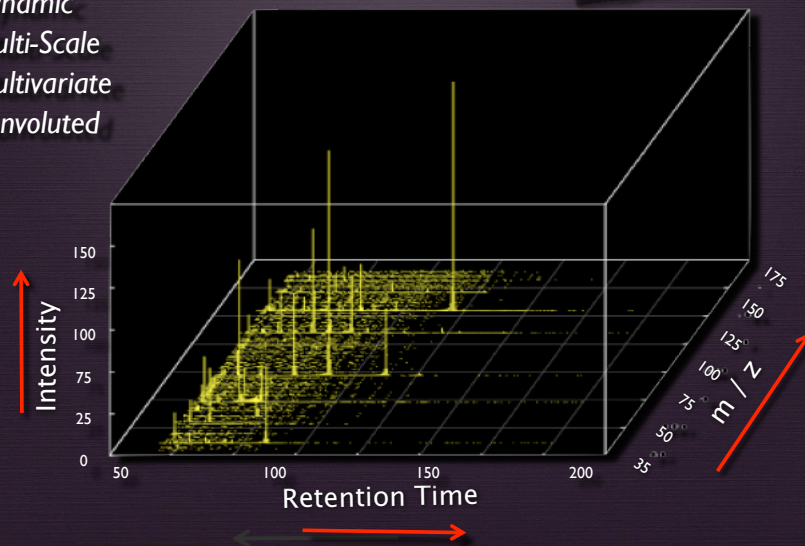
X-Metabolomics  
File Alignment Filtering MassMiner Help  
New Open Save Settings Reload Print BatchAlignment



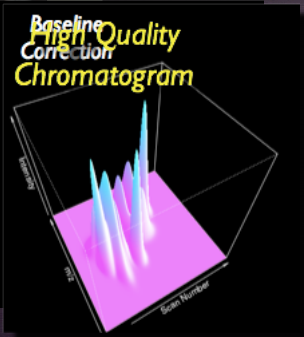


## Landscape ...

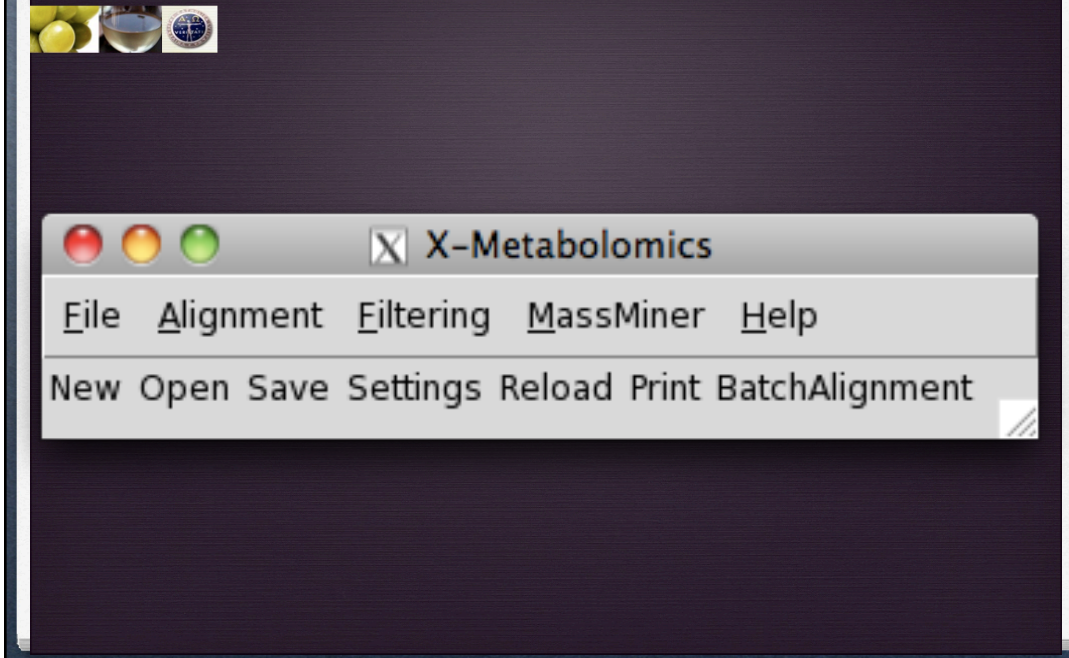
- Dynamic
- Multi-Scale
- Multivariate
- Convoluted



## Mass Spectroscopy Signal Processing







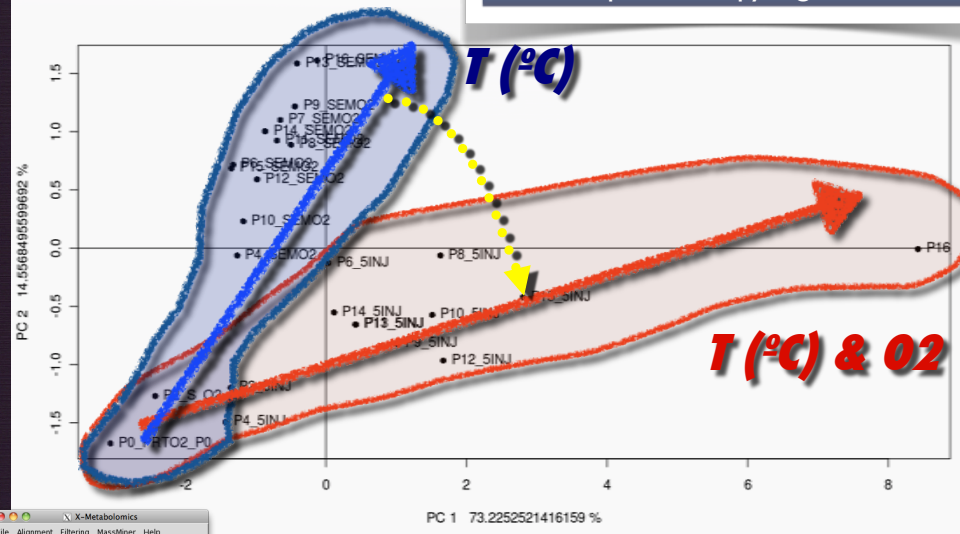
A spiral-bound notebook page with a dark background. At the top left, there are small icons of lemons, a beaker, and a globe. The main title is "Mass Spectroscopy Signal Processing". Below it, the text reads "Correlation Between Fragments : Clustering Non-biological components" and "Tikunov, Y., et al. (2005). Plant Physiology, 139, 1125-1137".

The left side features a dendrogram with a vertical axis labeled "distance". The dendrogram branches are colored: a blue triangle labeled "Robust Signal" and a yellow triangle labeled "Noise".

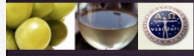
The right side features a "Cluster Dendrogram" with a vertical axis labeled "Robust Signal" and "Noise". The dendrogram shows a complex branching structure with a dense black area representing the signal.



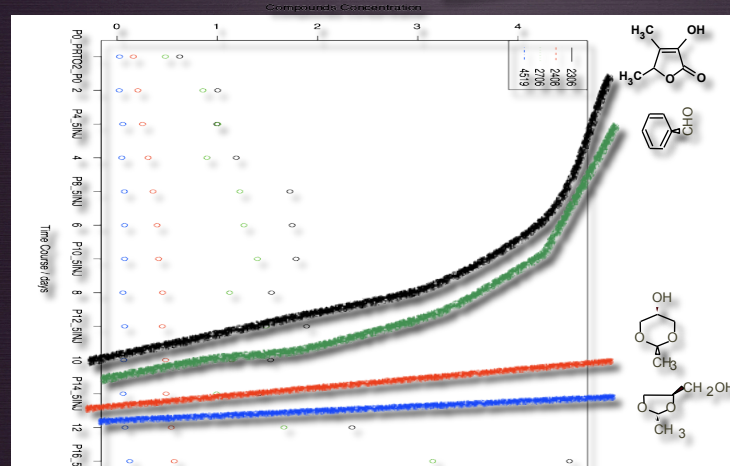
# Mass Spectroscopy Signal Processing



X-Metabolomics  
File alignment Filtering MassMiner Help  
New Open Save Settings Reload Print BatchAlignment



# Non Target : Mass Expression



Mass Expression

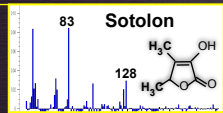
X-Metabolomics



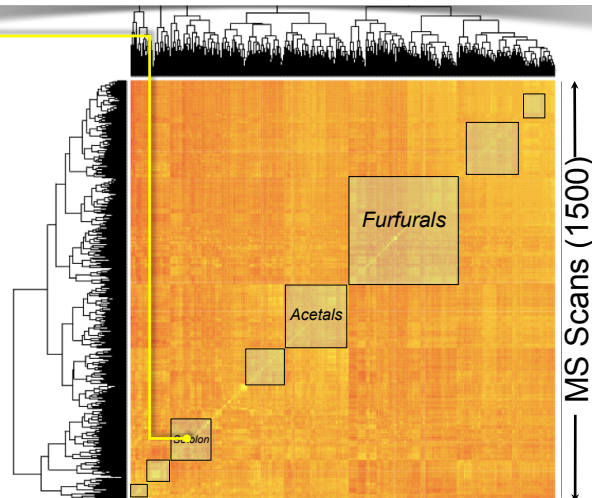
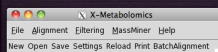
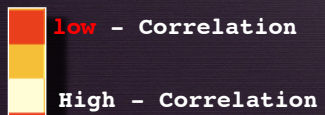


# Non-Target Approach : "Clustering" all MS

MS Scan : Mass Spectra  
example n° : 4519

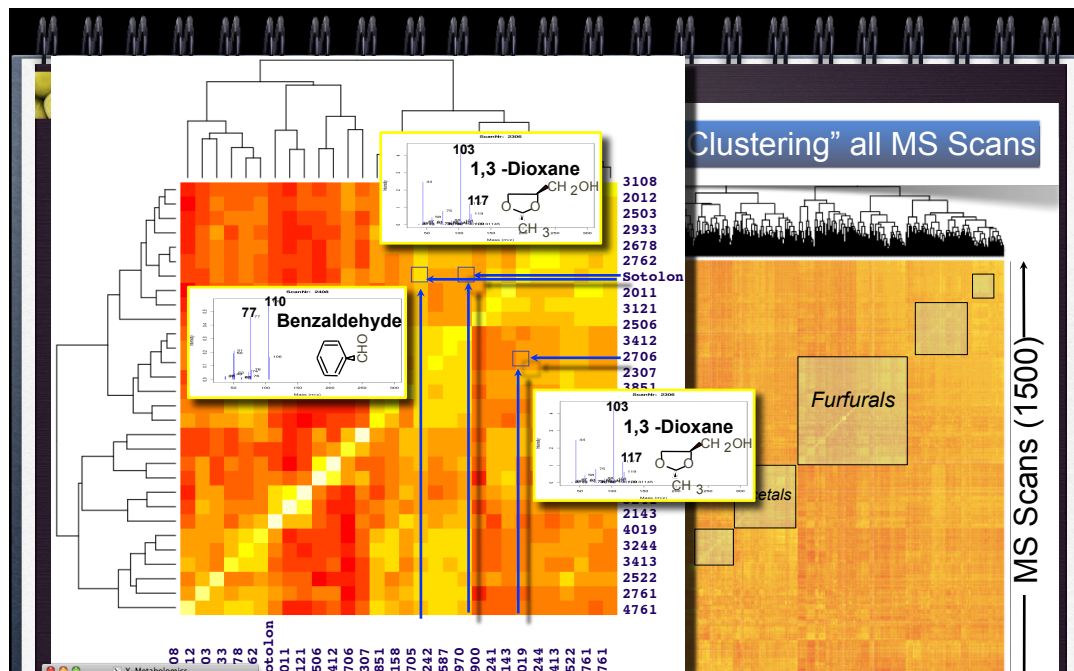


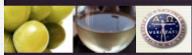
## "Pathway Reconstruction"



MS Scans (1500)

MS Scans (1500)

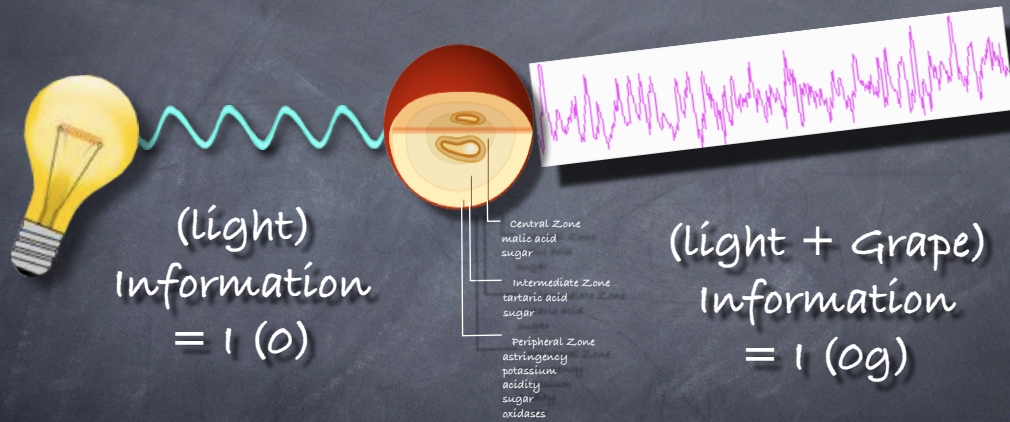




# The Grapes



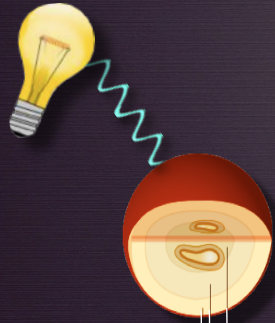
## Photonics : Molecular Information



$$\text{(Grape) Information} = 1 (0g) - 1 (0)$$



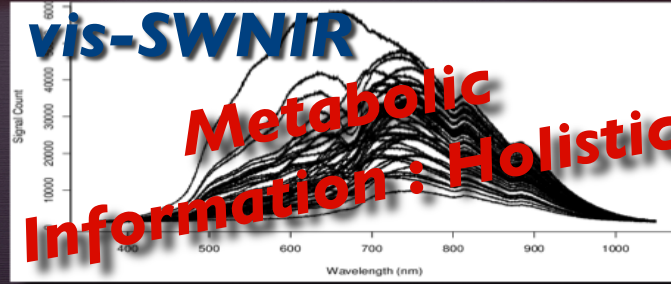
## Photonics : Molecular Information



Central Zone  
malic acid  
sugar

Intermediate Zone  
tartaric acid  
sugar

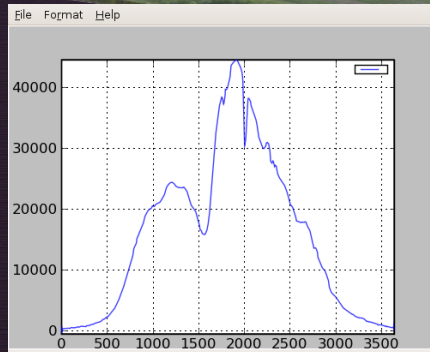
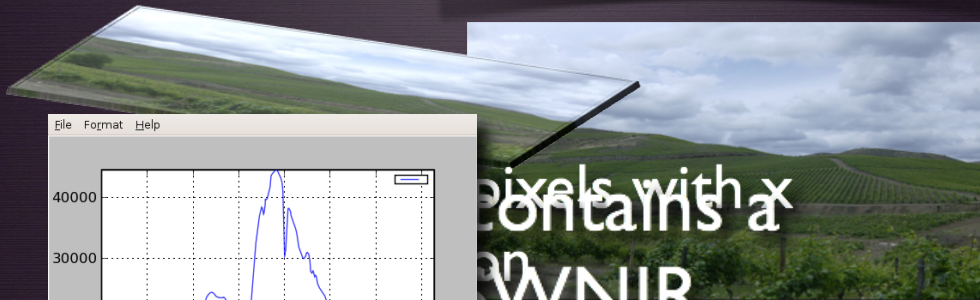
Peripheral Zone  
astringency  
potassium  
acidity  
sugar  
oxidases



### Complex Fingerprinting :

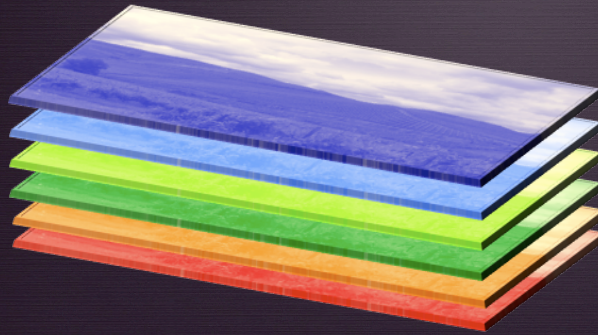
- Convoluted Information
- Advanced Computational Signal Processing, Feature and Pattern Recognition

## What is Hyper-spectral Imaging?





## What is Hyperspectral Imaging?



- Spatial Information for each time,
- Time Course Resolution,
- Each point of the field is a spectra,
- Allows high discrimination,
- Maturation Monitoring...



Movie Making...

Imaging : vis-SWNIR

