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Laboratory of Enology

Preliminary study of flavour compounds as oxidation markers in bottled white wines

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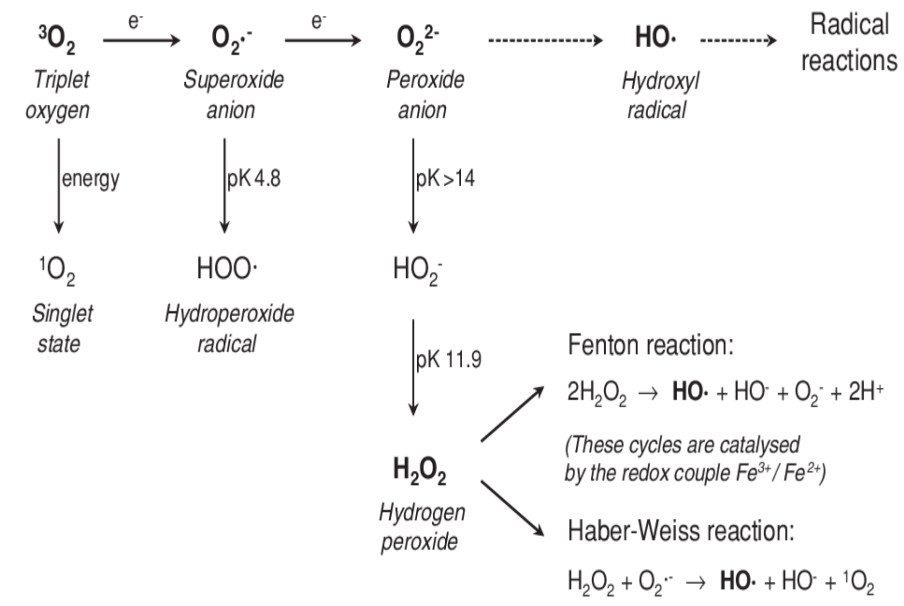
Wine bottle ageing



Forms of reactive oxygen

1. The degree of exposure of white wine to oxygen is an important factor for the formation of unwanted off-flavors.

a. Minor exposure results in a loss of fruity aroma,

b. Greater exposure leads to chromatic change (browning)

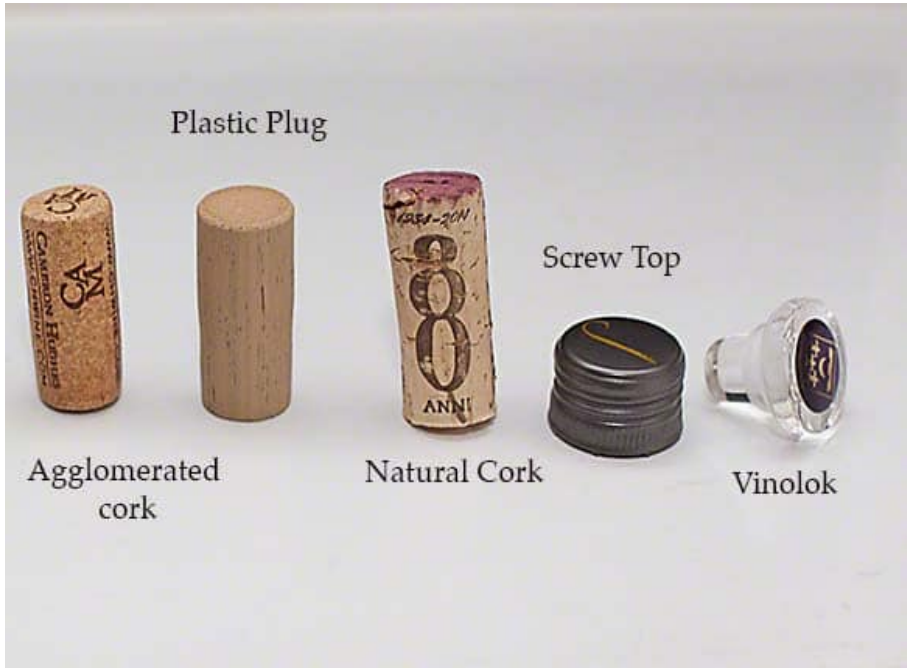
Wine corks

Wine closures

1. Mechanical properties
2. Oxygen permeability
3. Homogeneity
4. Sensorial neutrality

Wine Corks

Different levels of permeability in relation to the oxygen requirements of each wine (Oxygen Transfer Rate OTR)



Aims

1. To study the oxidation evolution of white wines in relation to the oxygen transfer rates of two different corks
2. To identify specific flavor quality indicators
3. To construct a mathematical model-based prediction of ‘acceptable’ oxidation levels

Experiment

SAMPLES

- **Three varieties of white wines:**

  Assyrtiko, Malagouzia, Sauvignon Bl.

- **Two types of agglomerated corks:**
  - P0.15 = **0.0008** cm^3/day
  - P0.35 = **0.0019** cm^3/day

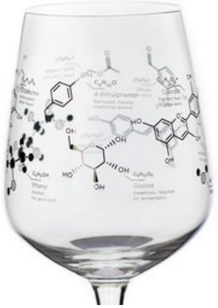
- **Stored at**

  At 20°C in the dark for 12 months

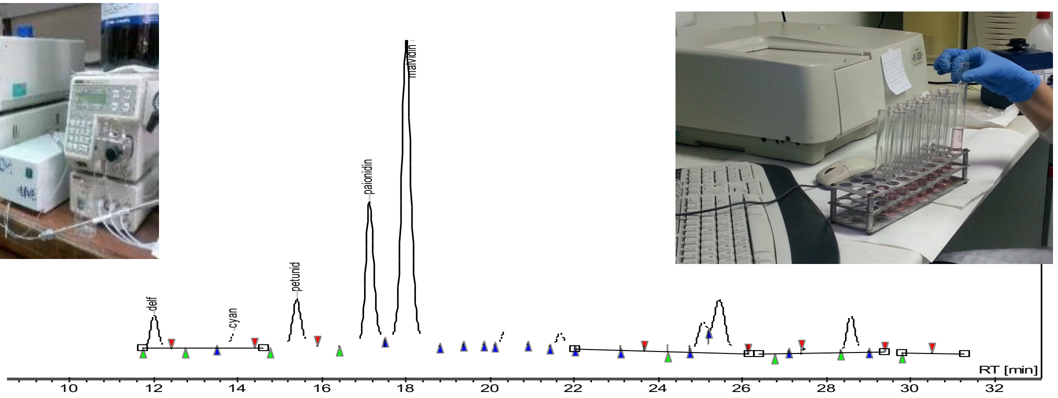
Wine storage

Experiment

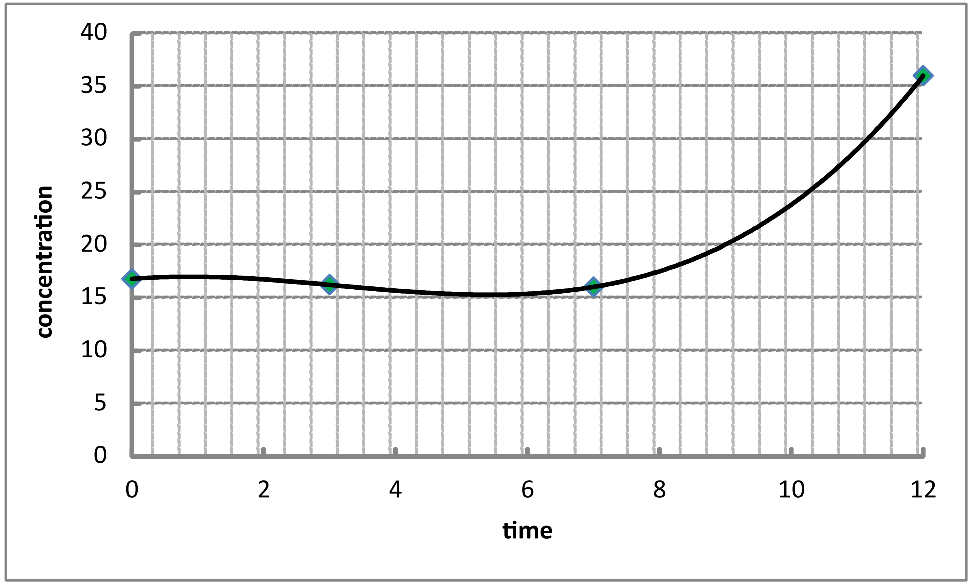
Analyses after: 0, 3, 6, 9 and 12 months of storage



- Total and free sulphur dioxide
- Acetaldehyde content
- Colour intensity
- Antioxidant activity
- Total phenols
- Accelerated browning test
- GC/MS analysis of volatile esters, alcohols and acids
- Sensory analysis

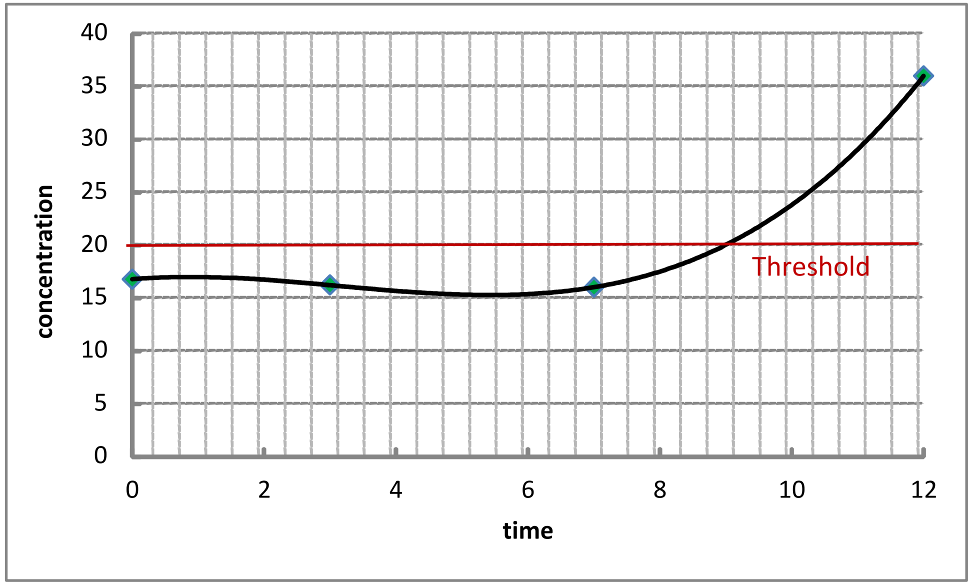


Mathematical Modeling: Identifying a marker



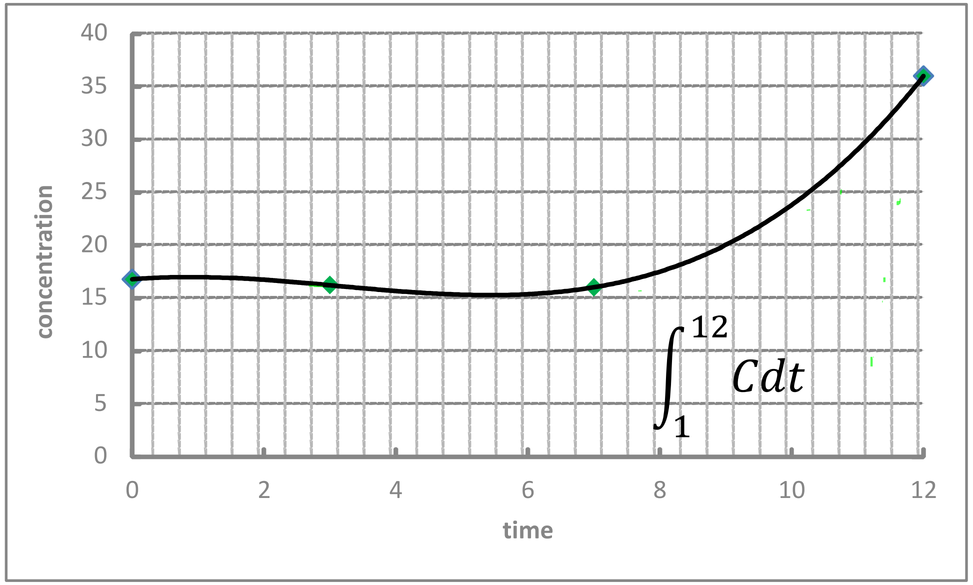
Concentration of an identified 'marker' over time

Mathematical Modeling: determine the threshold



'Concentration threshold'

Mathematical Modeling



'Intergration of the area under the curve'
AREA 1

Mathematical Modeling

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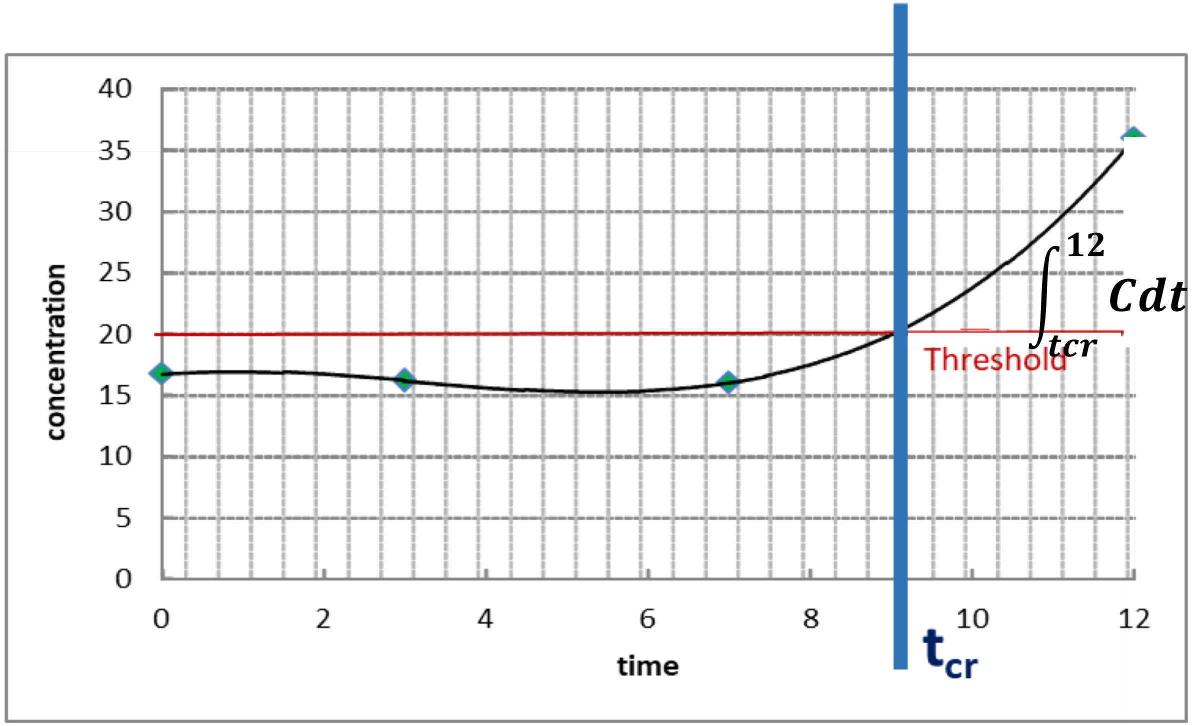


'Intergration of the area under the curve after tcr'
AREA 2

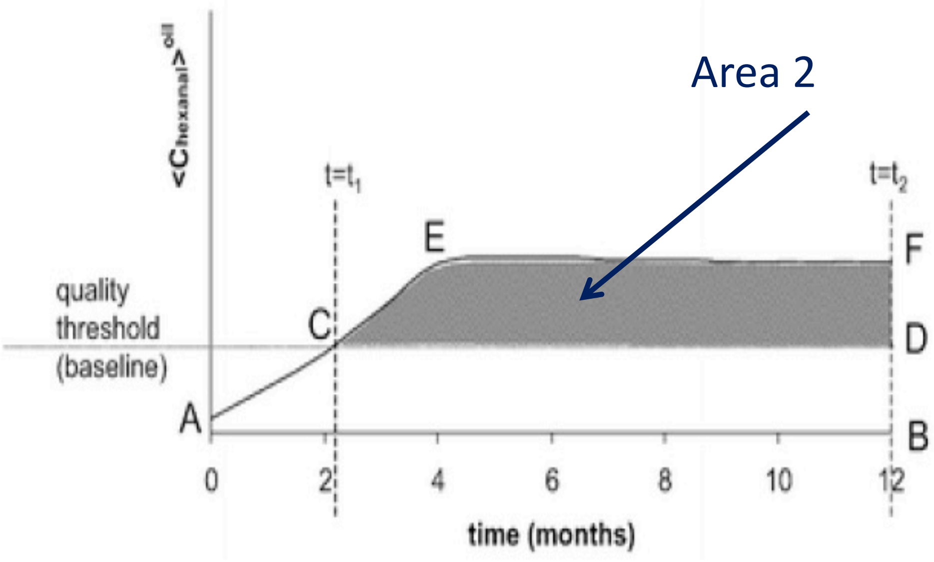
Mathematical Modeling

$$P = \frac{area\ 2}{area\ 1} = \frac{\int_{tcr}^{12} C dt}{\int_{1}^{12} C dt} \qquad (1)$$

$$P_{safe} = 1 - \frac{area\ 2}{area\ 1} = P_{safe} 1 - \frac{\int_{tcr}^{12} C dt}{\int_{1}^{12} C dt} \qquad (2)$$

Probabilities of the wine loosing (1) and not loosing its quality (2) by the end of its shelf life

Mathematical Modeling: Identifying a marker



Graphical representation of parameters used in Eq. 1

Results: Monitoring oxidation

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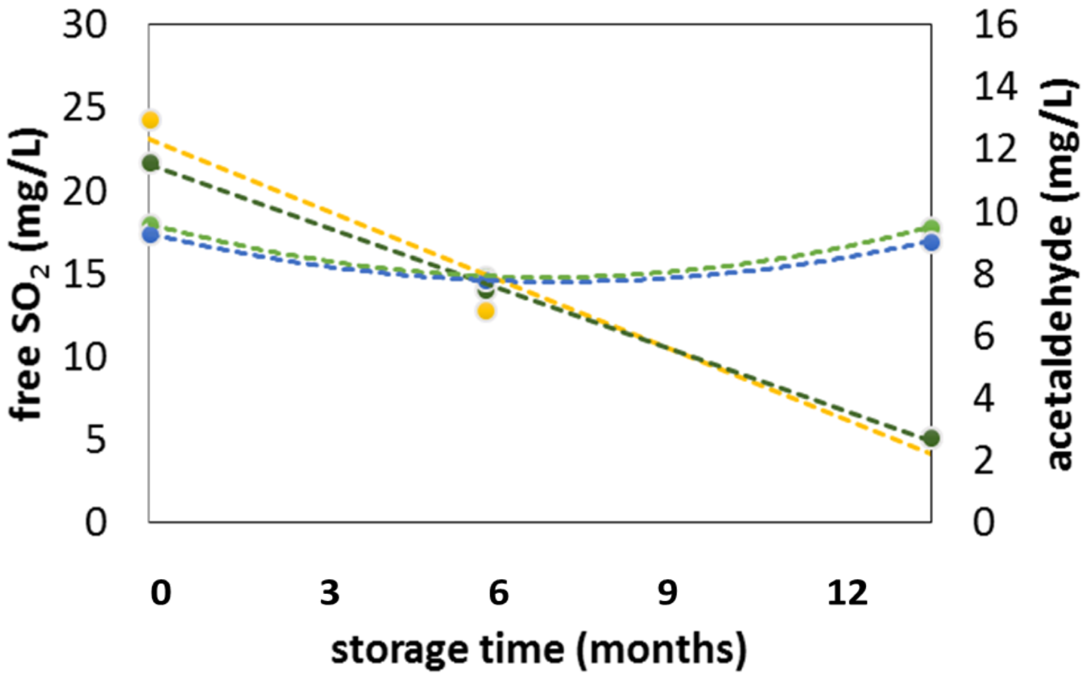


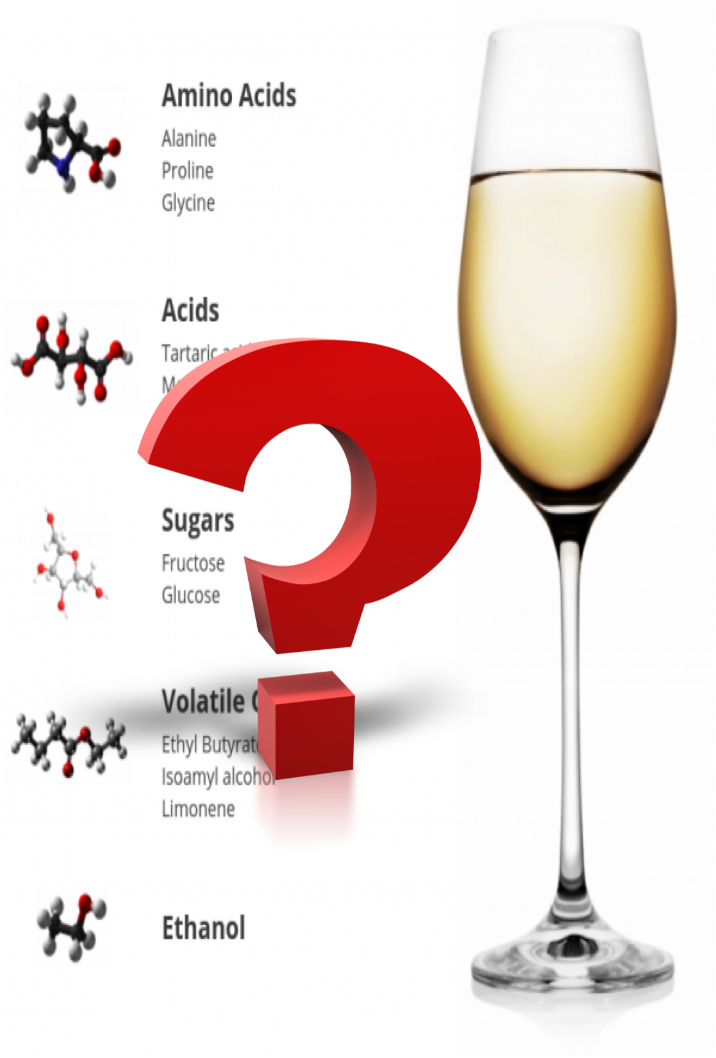
Free SO_2 and acetaldehyde contents during 12 months of storage

Table 1. Slopes of free SO_2 and acetaldehyde contents evolution curves

	20°C	
	P0.15	**P0.35**
Free SO_2	-2.7001	-2.37001
Acetaldehyde	0.13602	0.11632

1. Linear (kx) **2.** Polynomial (kx^2)

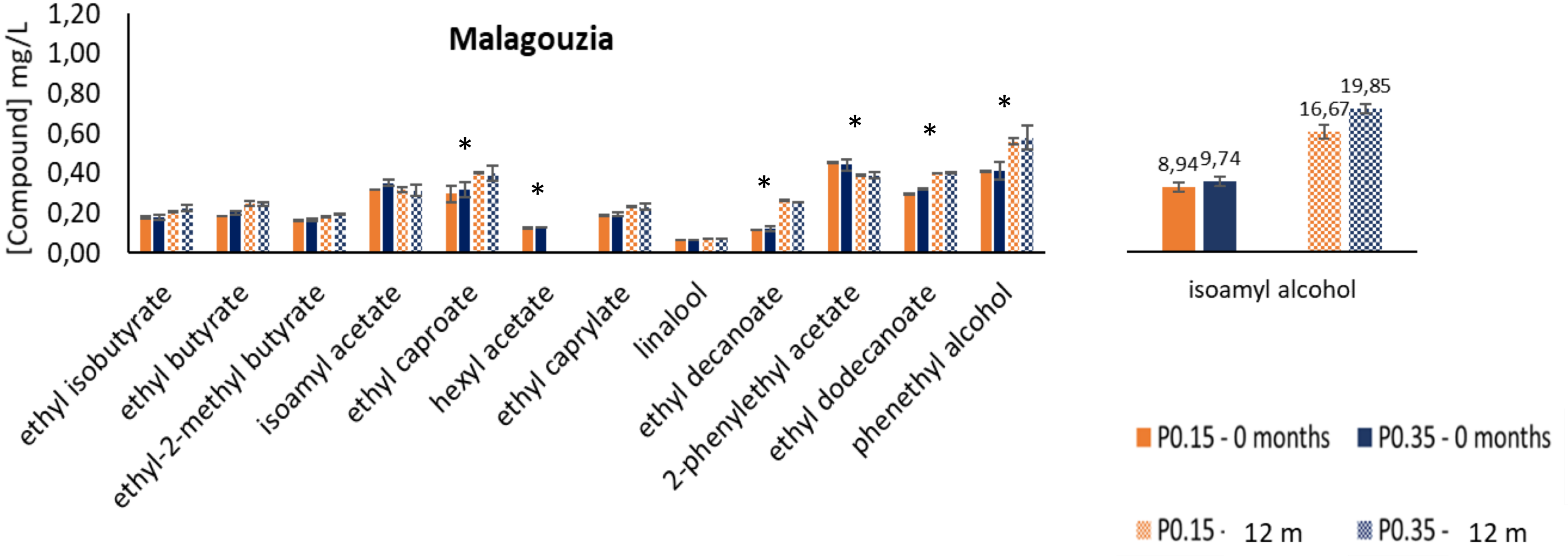
Results: Identifying the 'marker'



Criteria for the identification

1. ***Common compound among the different samples***
2. ***Significant difference in its content between the beginning and the end of the study and between the two corks***
3. ***Higher evolution slope***

Results: Malagouzia



Volatile concentration of Malagouzia wines at 0 and 12 months of storage

Results: Sauvignon Blanc

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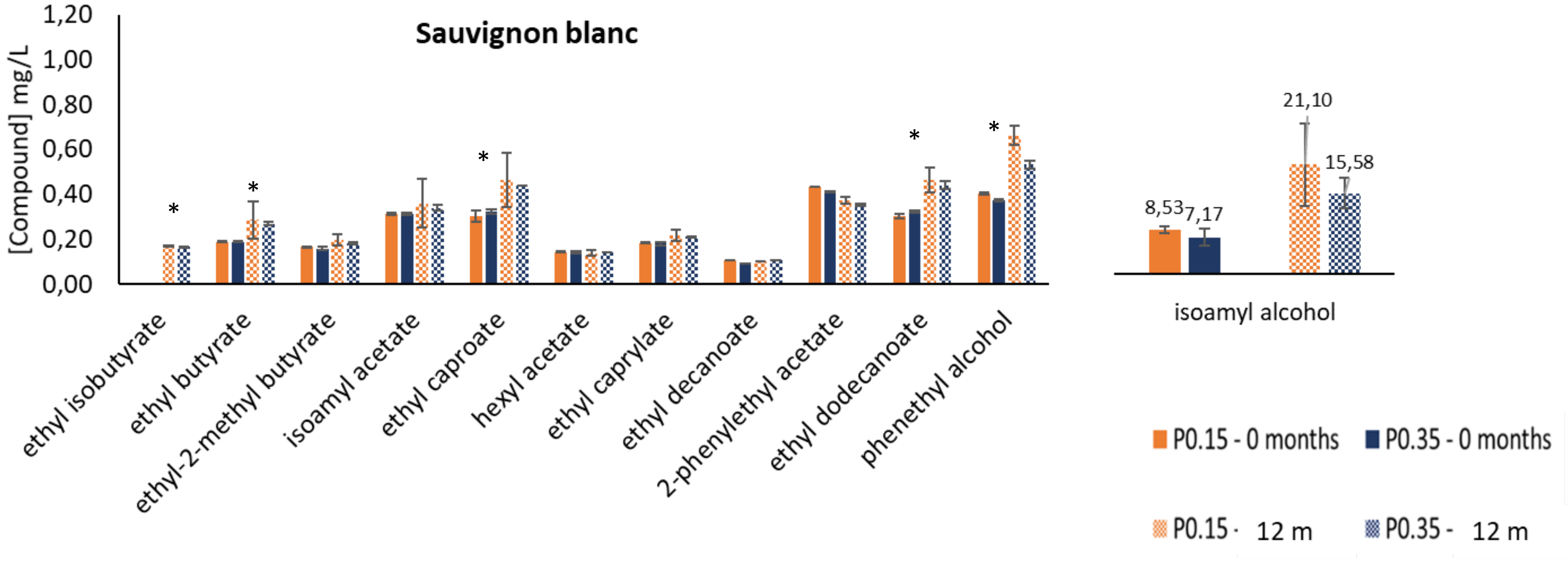

Volatile concentration of Sauvignon blanc wines at 0 and 12 months of storage

Results: Assyrtiko

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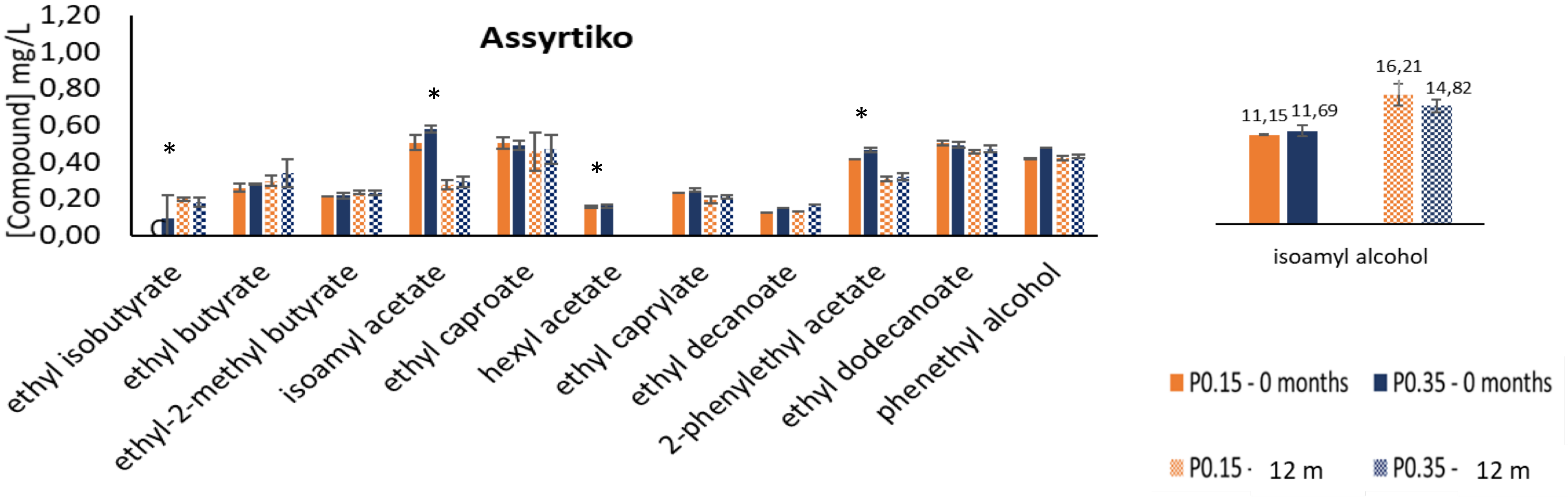

Volatile concentration of Assyrtiko wines at 0 and 12 months of storage

Results: identifying the 'marker'

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Table 2. Summary of the indicative ester and higher alcohol markers for the oxidative alterations occurring within the wines according to variety.

Malagouzia	Sauvignon Blanc	Assyrtiko
Ethyl caproate	Ethyl caproate	Isoamyl acetate
Ethyl decanoate	Ethyl butyrate	2-phenethyl acetate
Ethyl dodecanoate	Ethyl dodecanoate	Hexyl acetate
Hexyl acetate	Ethyl Isobutyrate	Ethyl Isobutyrate
2-phenethyl acetate	Phenethyl alcohol	
Phenethyl alcohol		
Isoamyl alcohol	Isoamyl alcohol	Isoamyl alcohol

Results: Slopes

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Table 3. Slopes of the evolution of the concentration of esters and higher alcohols during one year according to the type of cork and the variety.

wine	cork	ethyl isobutyrate	ethyl butyrate	ethyl-2methyl butyrate	isoamyl acetate	isoamyl alcohol	ethyl caproate	hexyl acetate	ethyl caprylate	ethyl decanoate	2phenyl ethyl acetate	ethyl dodecanoate	phenethyl alcohol
Assyrtiko	P0.15	0.002	0.0002	-0.00006	0.0004	0.0541	0.00002	0.0012	0.0001	-0.000006	0.0052	0.00002	0.006
Assyrtiko	P0.35	-0.0038	-0.0002	-0.0004	0.0004	0.0552	0.0001	0.002	0.0006	0.0002	-0.008	0.00001	-0.0026
Malagoyzia	P0.15	4E-07	0.0002	0.0001	0.0008	0.004	0.0024	0.0014	-0.0001	-0.001	0.0006	0.0024	0.0028
Malagoyzia	P0.35	-0.002	-0.002	-0.0028	0.0012	0.0208	-0.0016	0.002	-0.0002	0.001	0.0008	-0.0016	0.0006
Sauvgnon B.	P0.15	0.0004	0.0001	-0.00001	0.001	0.0592	-0.0001	-0.00002	-0.0004	-0.0006	0.0026	0.0001	0.001
Sauvignon B.	P0.35	0.0026	-0.0002	-0.0001	0.002	0.1228	-0.0018	0.00001	-0.0006	-0.0006	0.0001	-0.0008	0.0026

Results: Determining the thresholds

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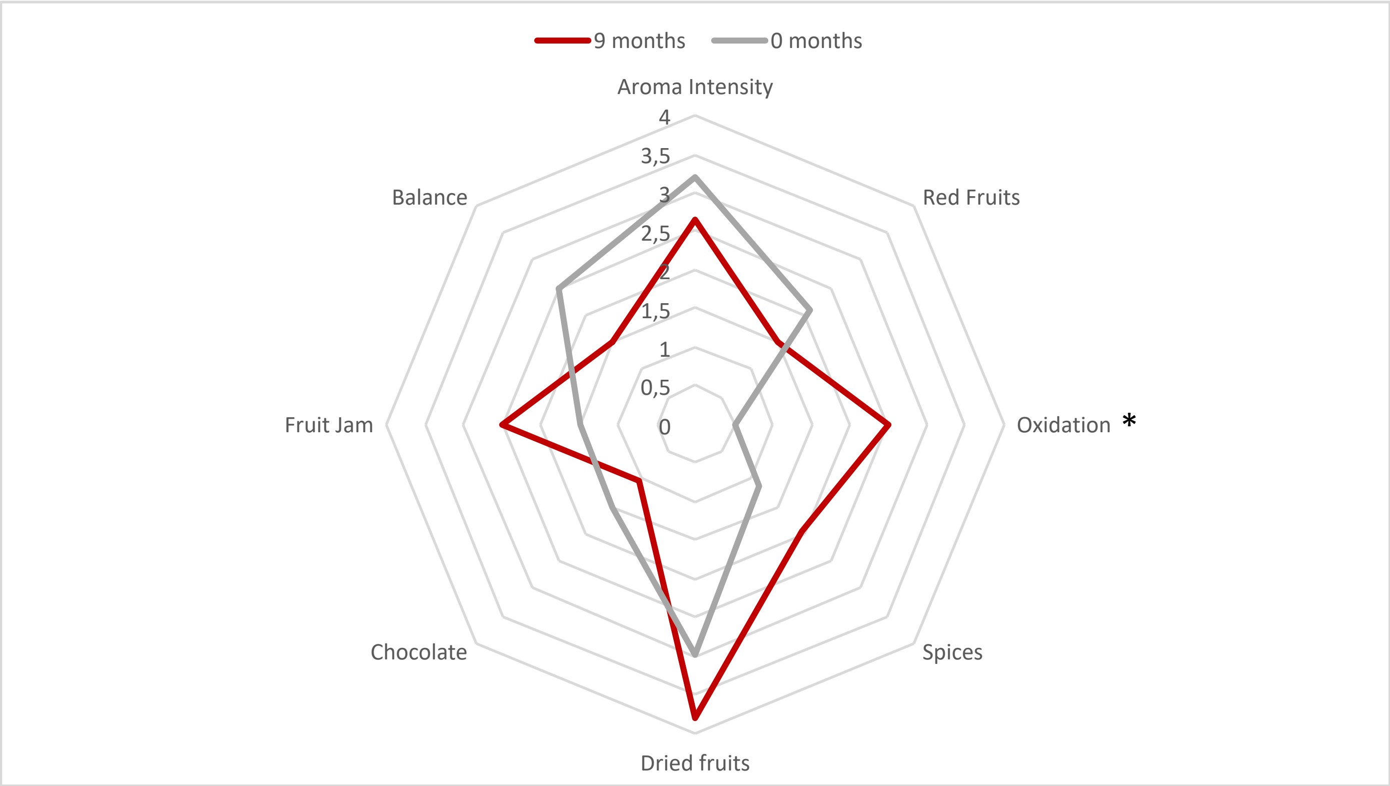
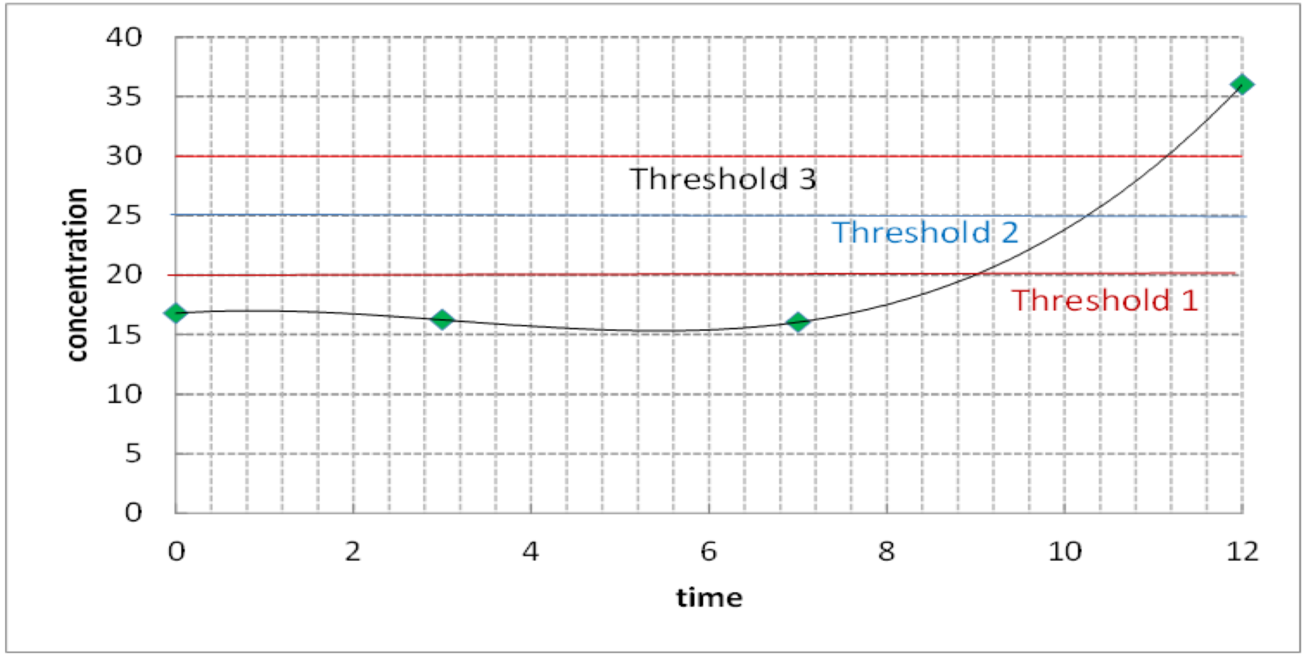


Sensory attributes of the wine samples

Results: Thresholds



Graphical representation of the identification of critical time in equation 2

Results: Equations

$$P_{safe} = 1 - \frac{\int_{time\_critical}^{end\_of\_period} C_{isoamyl\_alcohol}(t)dt}{\int_{0}^{end\_of\_period} C_{isoamyl\_alcohol}(t)dt} \quad (1)$$

$$P_{safe} = 1 - \frac{\int_{t_{cr}}^{12} C_{isoamyl\_alcohol}(t)dt}{\int_{0}^{12} C_{isoamyl\_alcohol}(t)dt} \quad (2)$$

Results: Psafe

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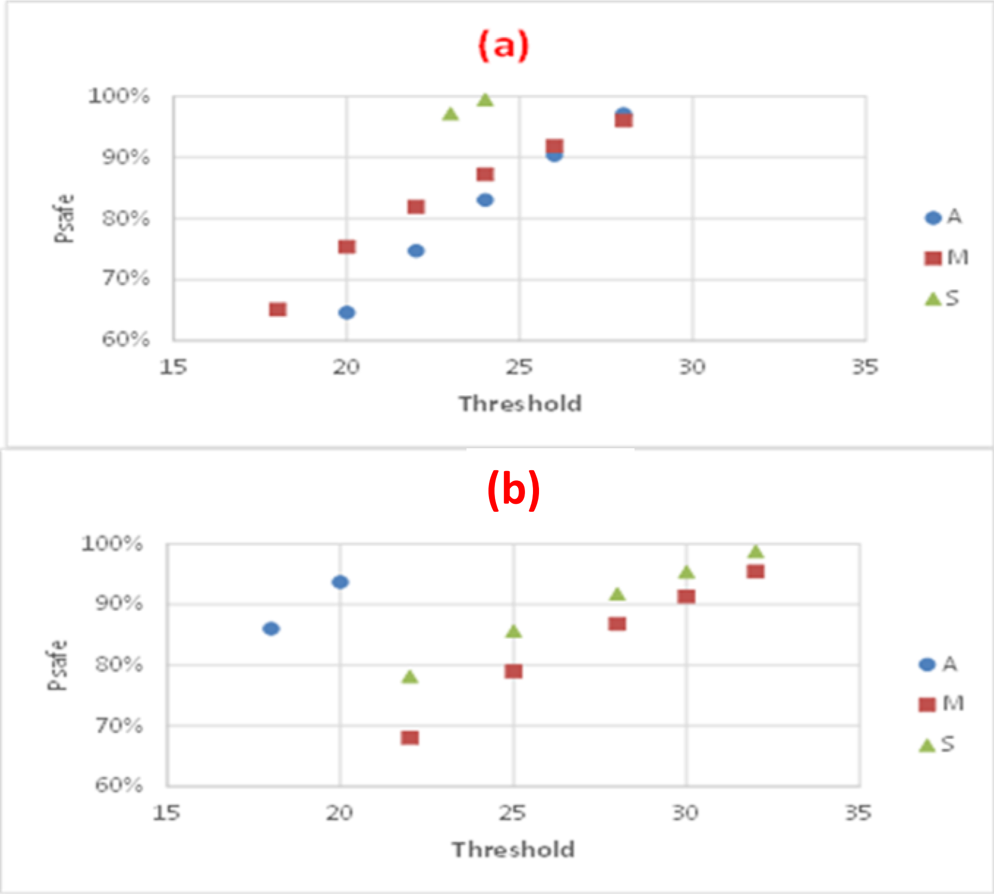
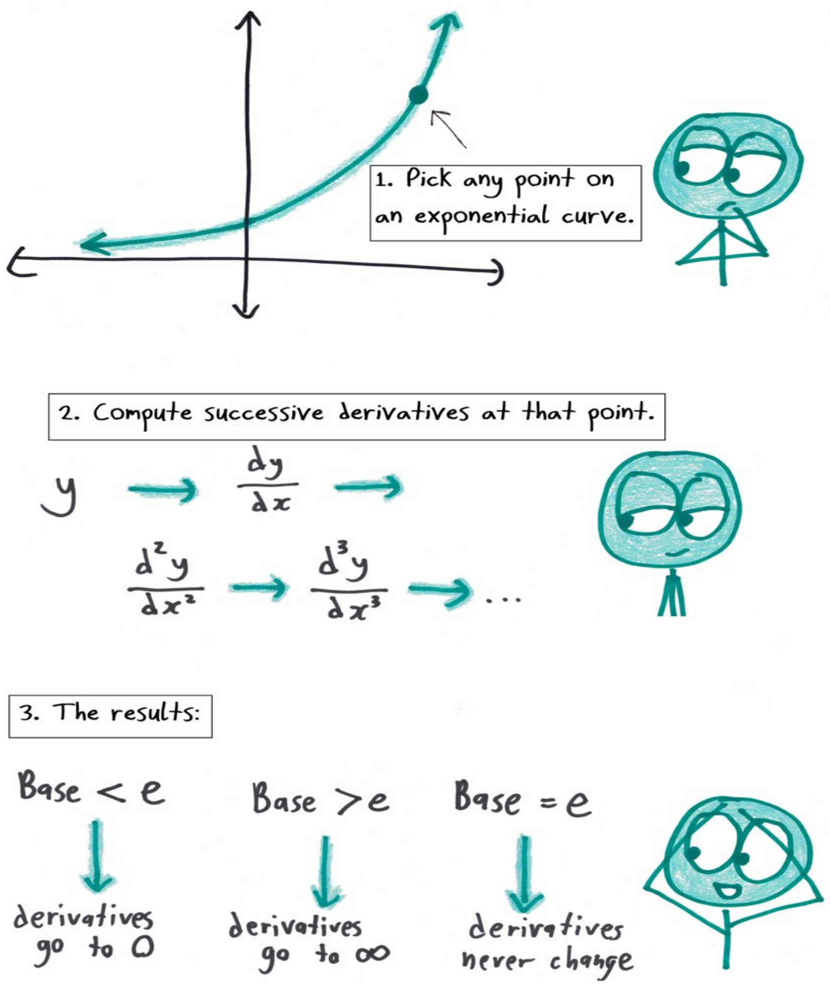


Effect of threshold value on P_{safe} for P0.15 cork (a), and P0.35 (b), and the three wine varieties (A-Assyrtiko, M-Malagouzia, S-Sauvignon blanc).

Week points



Arbitrariness in selection of:

1. Marker compound
2. Threshold value
3. ‘Acceptable’ wine quality level (oxidation, browning etc.)
4. Shelf life time

Conclusions

1. Isoamyl alcohol was identified as potential marker to monitor wine oxidation.
2. A mathematical model was applied for the calculation of the probability that the wine will have an acceptable quality at the end of its self life during a defined time period
3. A successful fit was obtained between model and sensory deriving shelf life predictions.

Thank you for your attention !!!