ADReM
Advanced Database Research & Modelling
University of Antwerp

biomina

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Antwerpen

Wine fluorescence excitation-emission matrix (EEM)
Data analysis towards universal modelling

Liu Youzhong, Coelho Christian, Gonsior Michael, Nikolantonaki Maria, Lucio Marianna, Schmitt-Kopplin Philippe, Gougeon Régis

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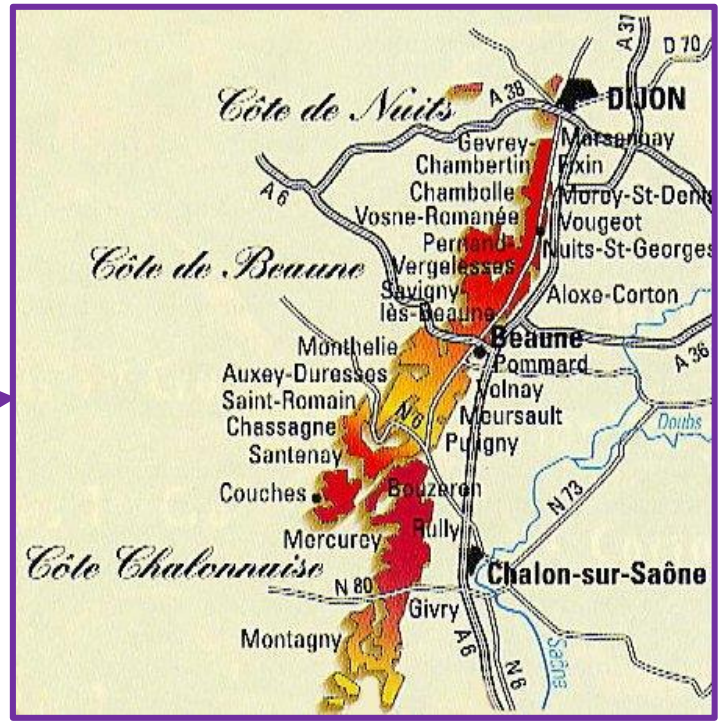
Burgundy, France



Wine and Vineyards

- Process Control
- Geography and Climate
- Microbiology
- Wine chemistry
- Health effect
- ….

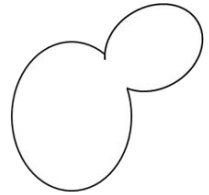
Don’t only drink me, observe me first !

Professional wine tasting

Acidity, Toasty, Oxidized, Buttery, Cheesy…

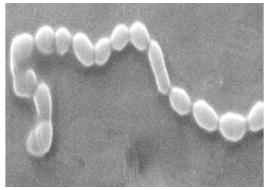
Winemaking practices ?



Viticulture → Pressing → Alcoholic Fermentation

Malolactic Fermentation → Oak barrel ageing from 6 to 24 months → Bottle ageing



Wine “Labels”

Winemaking practices ?

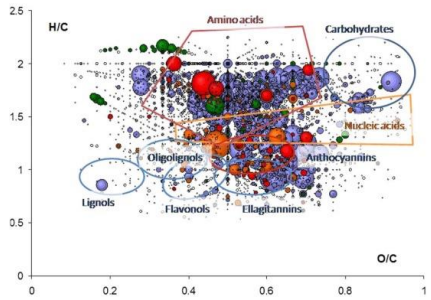
Biochemical complexity ?

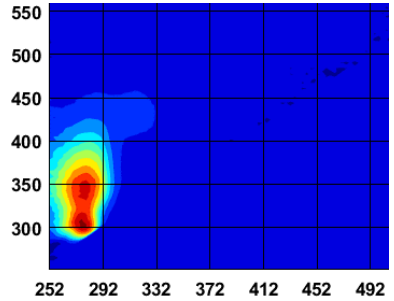
Spectroscopy & Spectrometry

- Infrared and UV-Vis spectroscopy
- Fluorescence spectroscopy
- Mass spectrometry
- Nuclear magnetic resonance (NMR)
- Electron paramagnetic resonance (EPR)
- …

Targeted (Molecule by molecule)

Non-targeted (Photographing)





Fluorescence excitation-emission matrix (EEMF) spectroscopy

Wine "Labels"

Winemaking practices ?

Biochemical complexity ?

Spectroscopy & Spectrometry

- Infrared and UV-Vis spectroscopy
- **Fluorescence spectroscopy**
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Targeted (Molecule by molecule)

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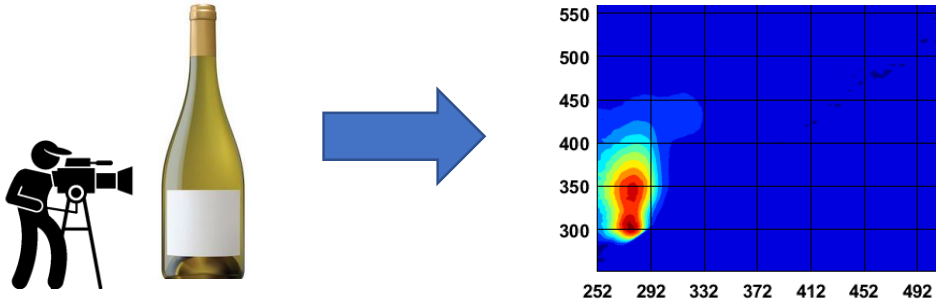
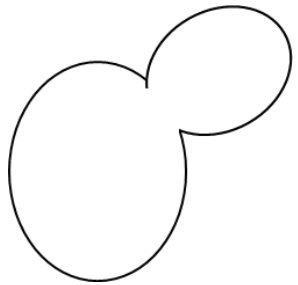
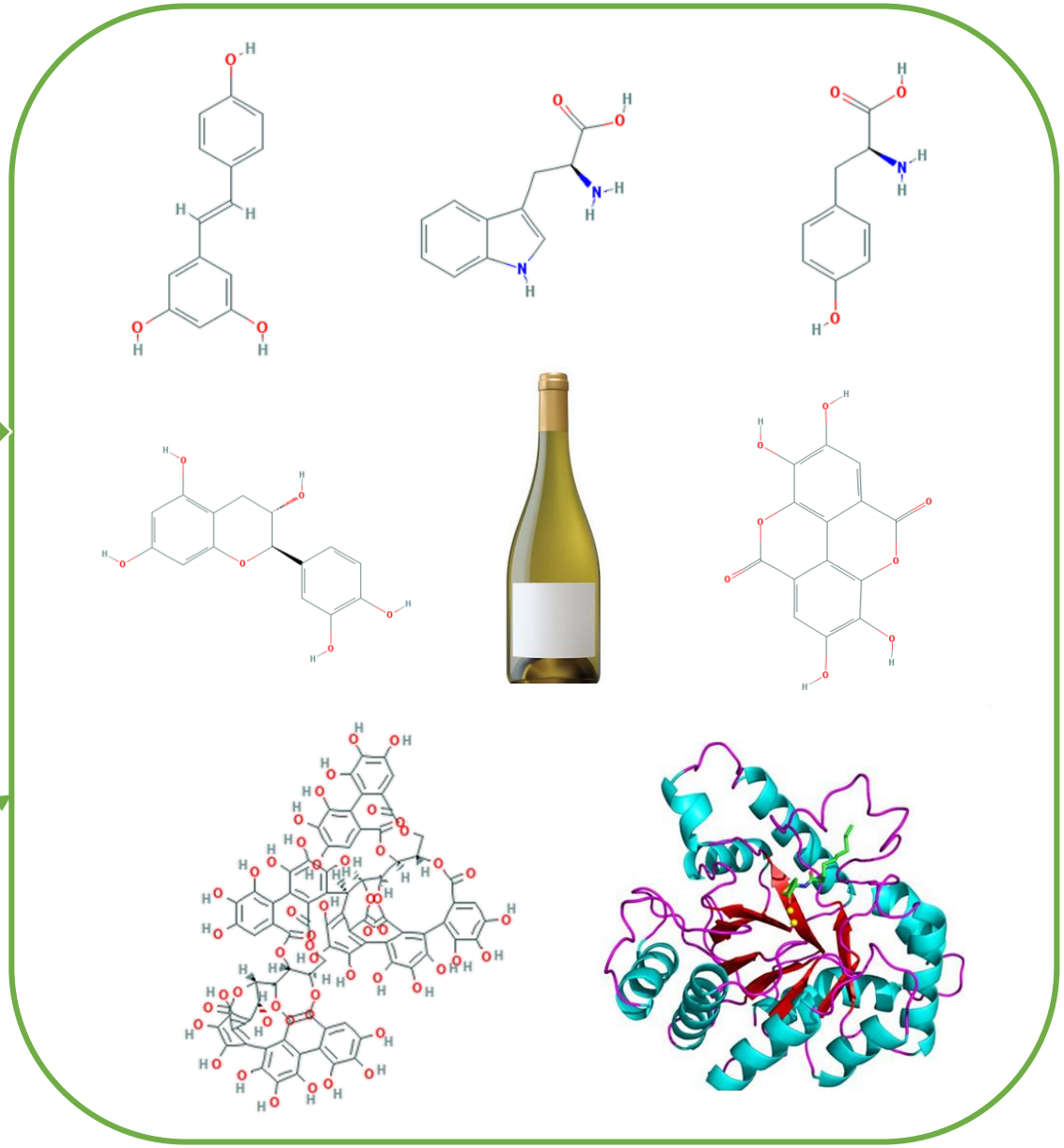
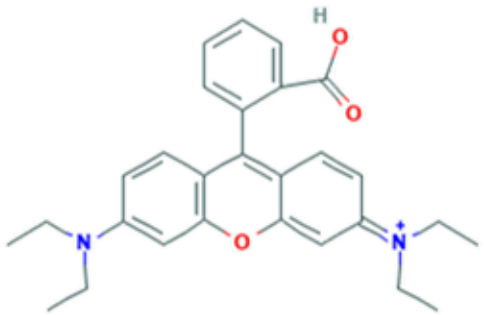


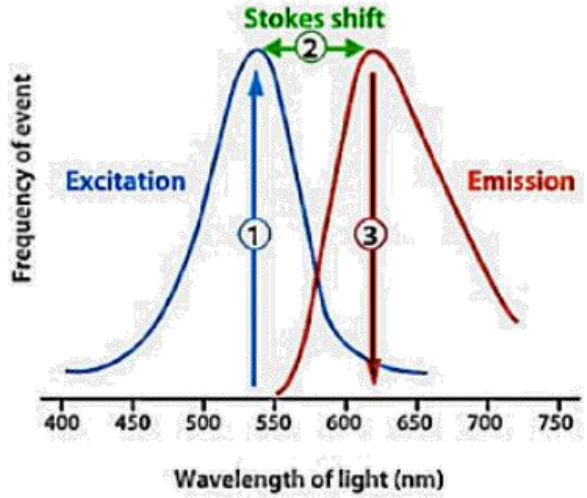
Wine fluorophores and their origins

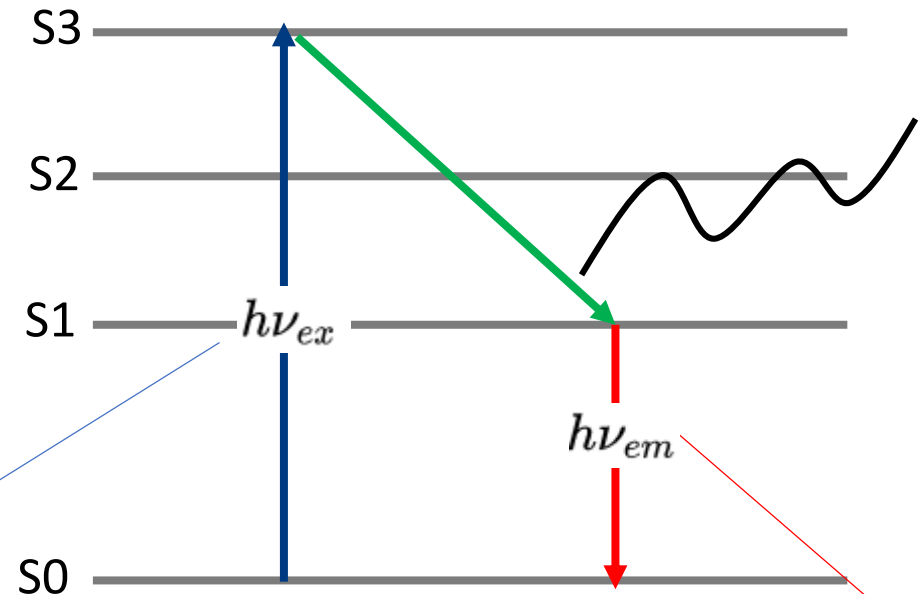




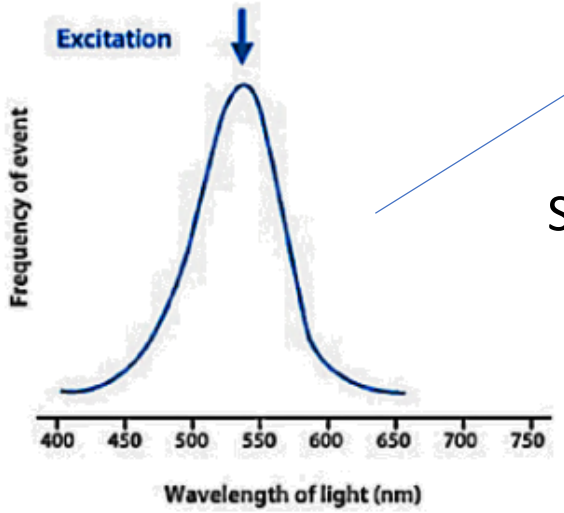
Recall of basic physics: fluorescence and fluorophore

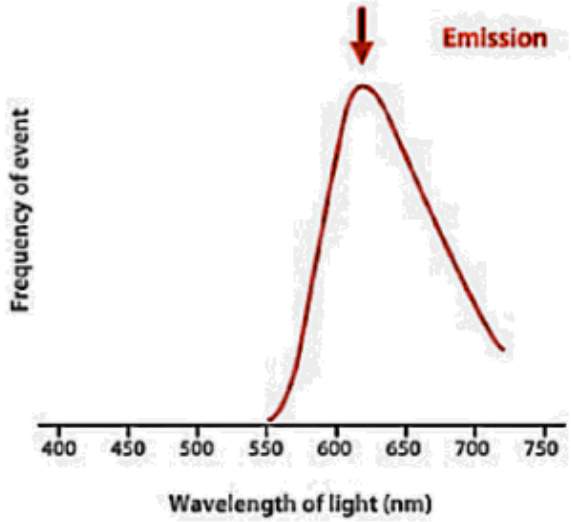




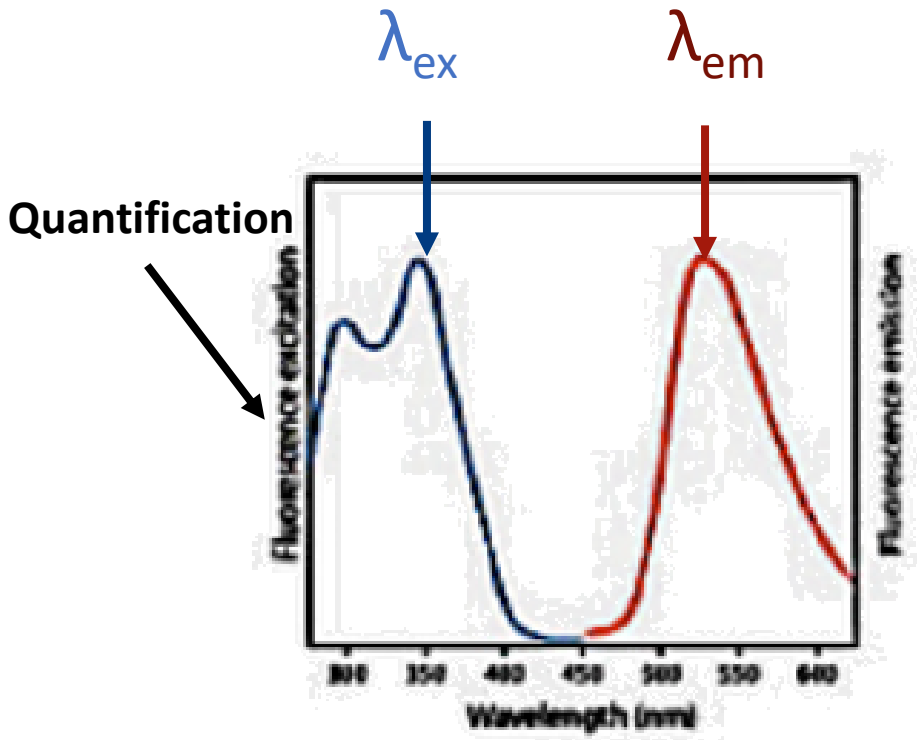


Energy Loss





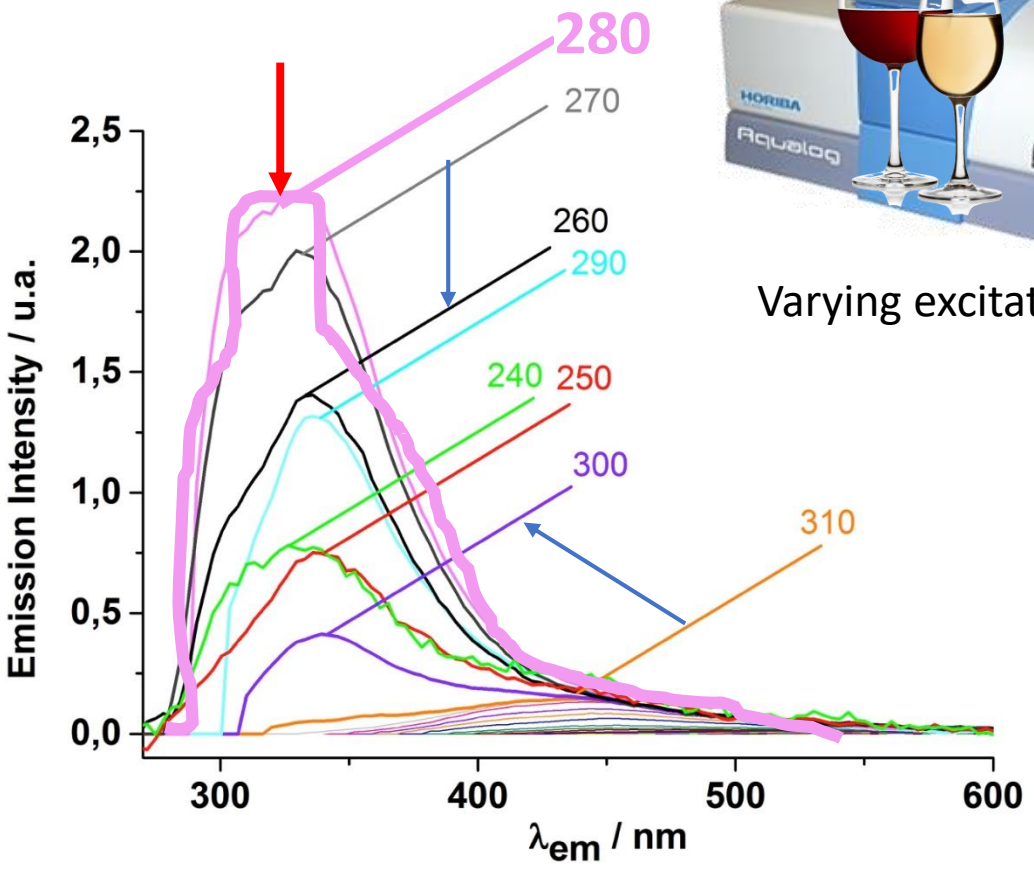
Recall of basic physics: fluorescence and fluorophore



λ_{ex} / nm	λ_{em} / nm	Wine compounds
260-280	320-420	Phenolic acids
260	310-360	Flavonols
280	320-360	Flavan-3-ols
280-320	400-480	Vitamins, Enzymes
280	305-360	Proteins

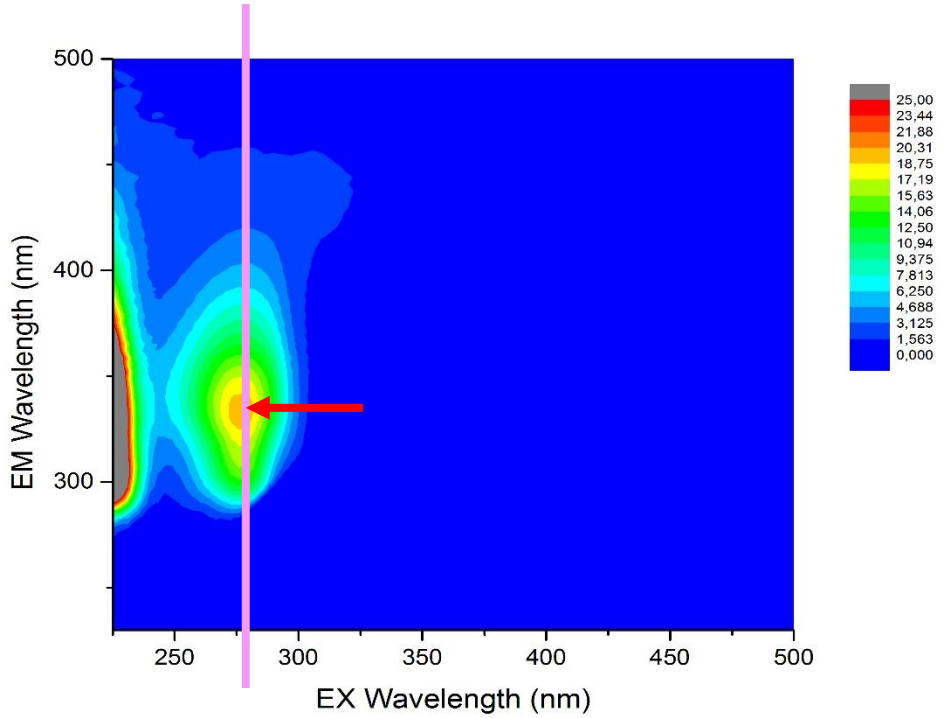
How about other excitation wavelengths ?

EEM spectroscopy: a non-targeted approach



Varying excitation λ

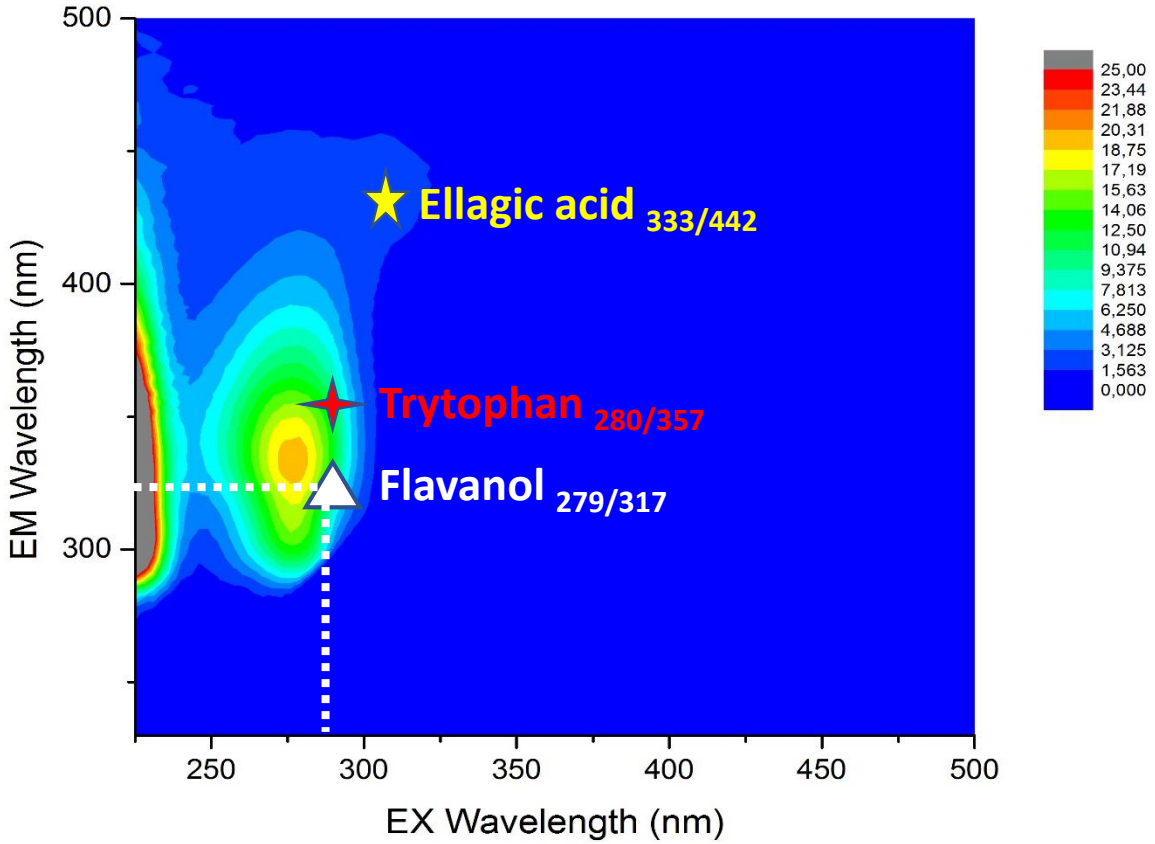
λ_{ex} = 280 nm

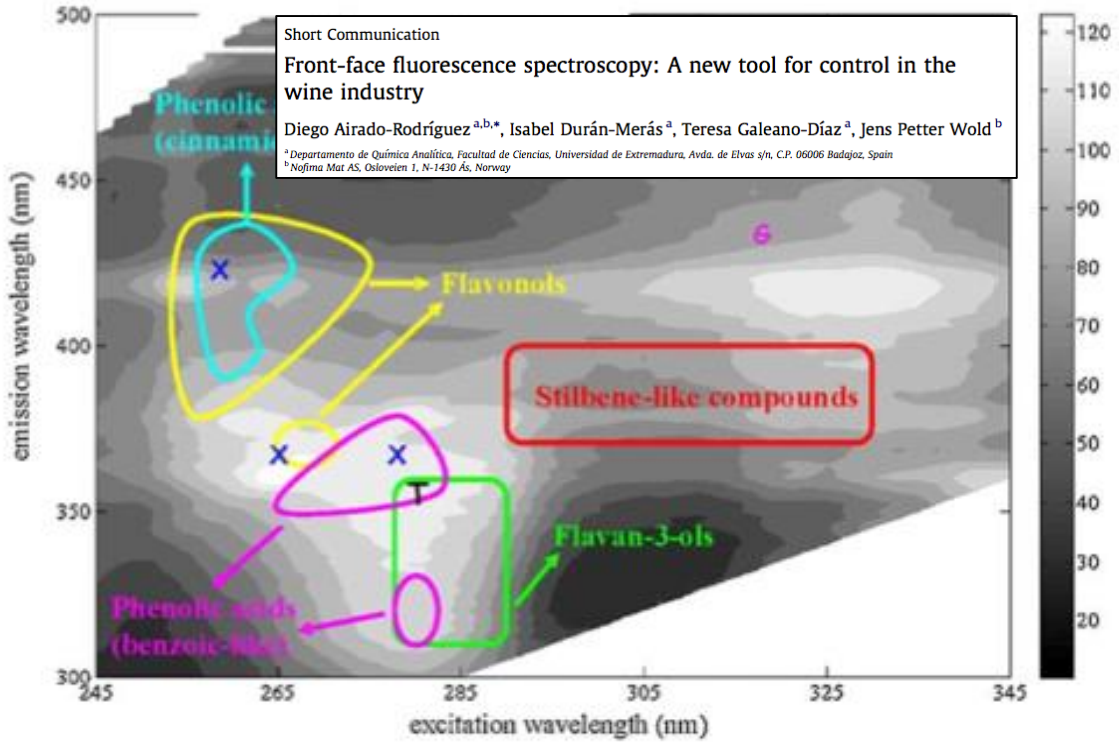


5 - 10 min

EEM = a 2D view of a fixed number of emission spectra acquired with varying excitation wavelength

Direct image interpretations and limits



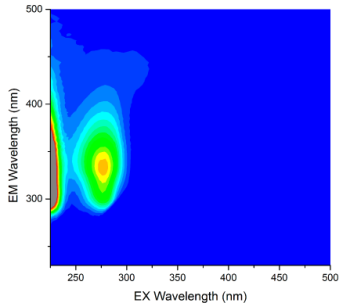


- Overlapping of fluorophores or fluorophore families
- Peak shift of fluorophores from sample to sample
- Ignoring information of other pixels

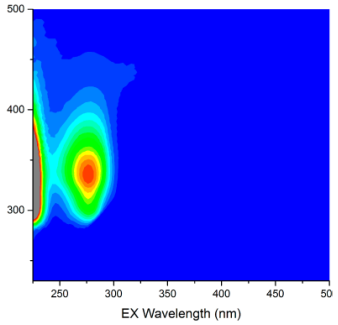
Difficult to Compare

Bioinformatics-driven image interpretations

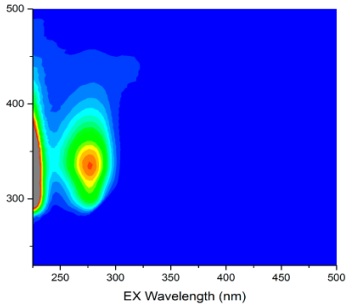
Wine A

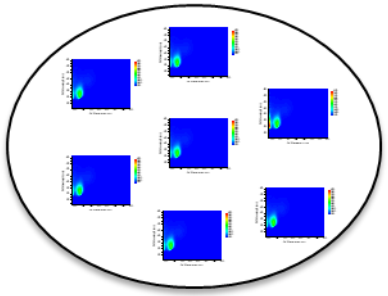


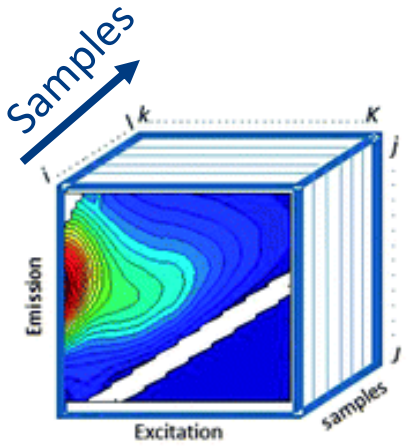
Wine B



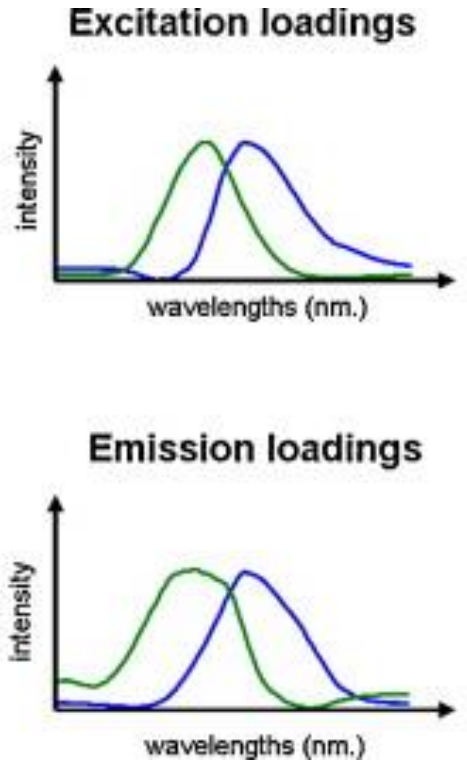
Wine C







PARAFAC



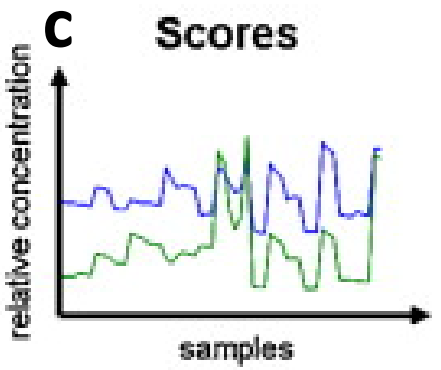
1st PARAFAC component

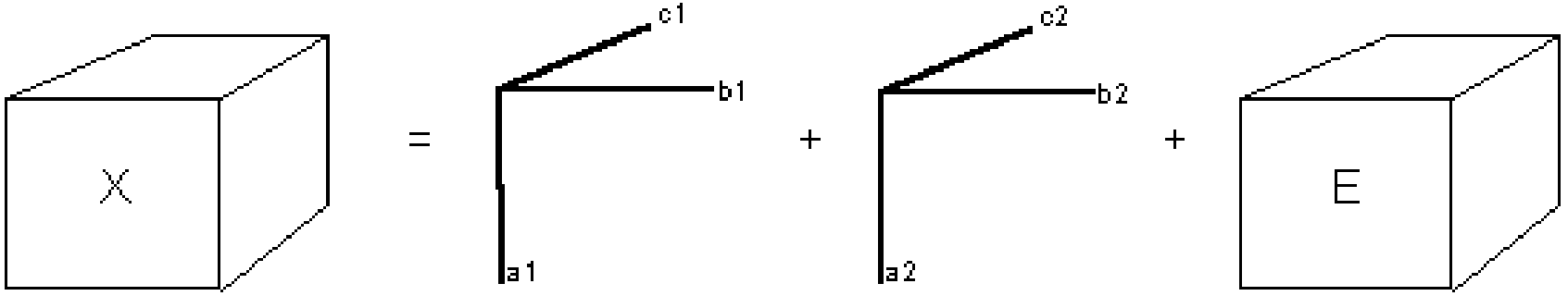
2nd PARAFAC component

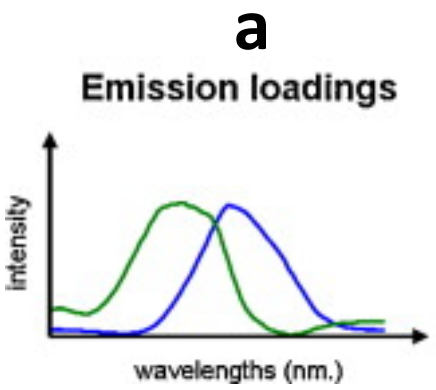
Parallel Factor Analysis (PARAFAC)

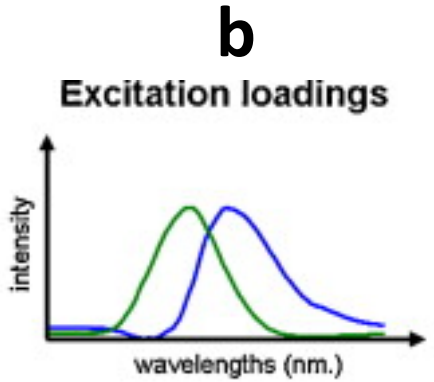
1st PARAFAC component

2nd PARAFAC component

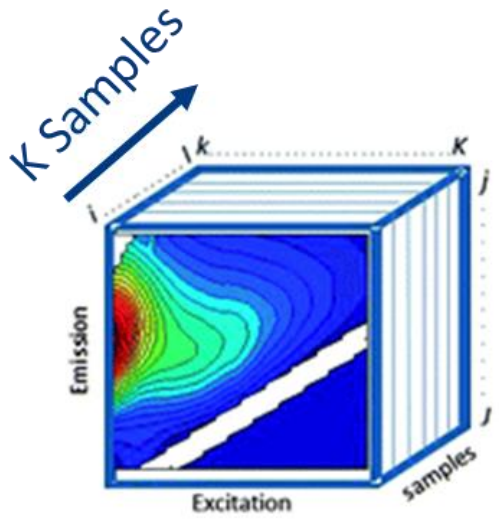








Parallel Factor Analysis (PARAFAC)

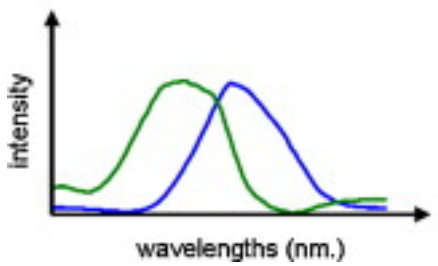


$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk}$$

F: number of components

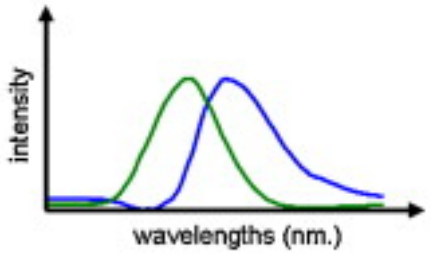
k = 1, …, K samples
i = 1,…, I wavelengths
j = 1,…, J wavelengths

Emission loadings



⊗

Excitation loadings



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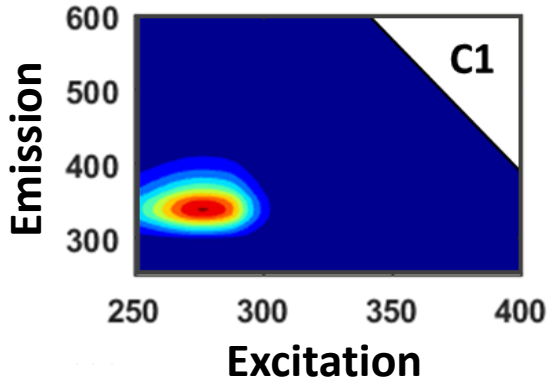
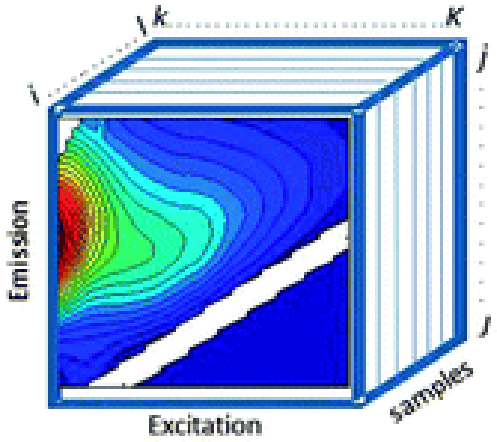
Loading fingerprint

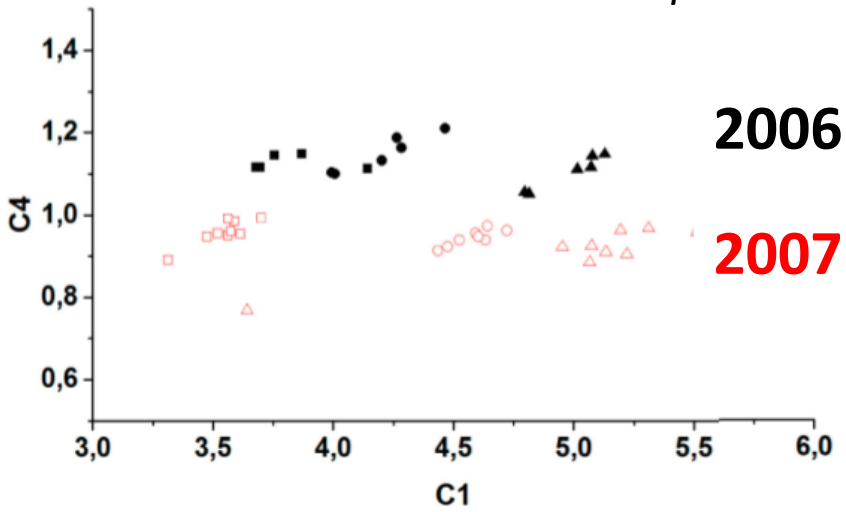


Bioinformatics-driven image interpretations



Scores/F_{max}

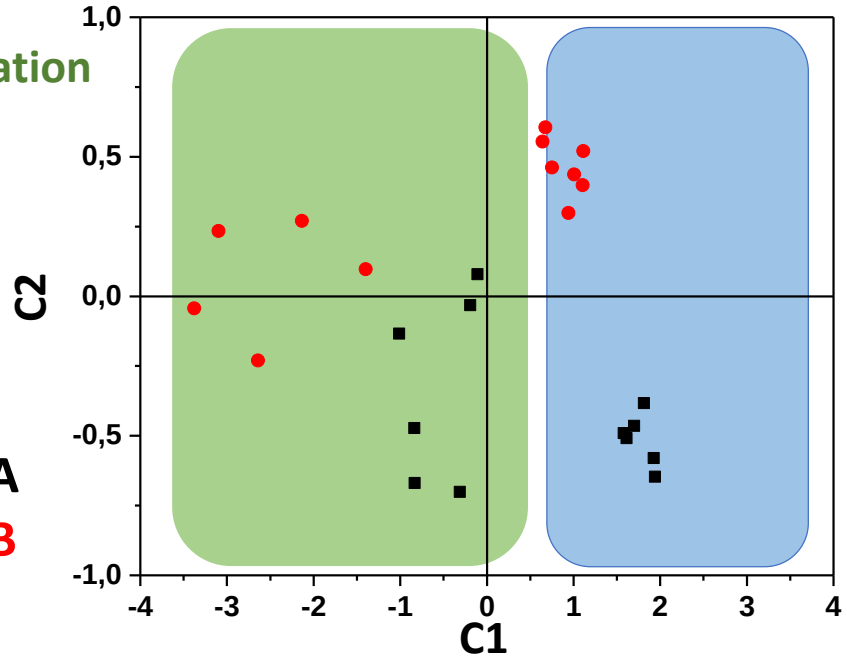
A point = A wine sample



2006

2007

Post-fermentation

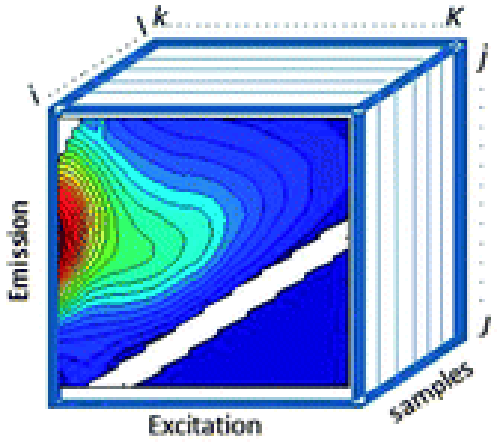


Winery A

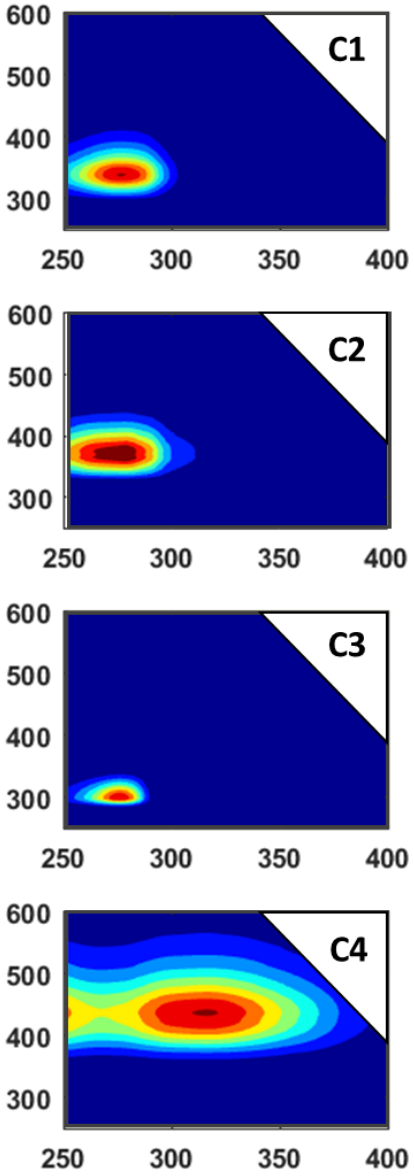
Winery B

During Ageing

Bioinformatics-driven image interpretations

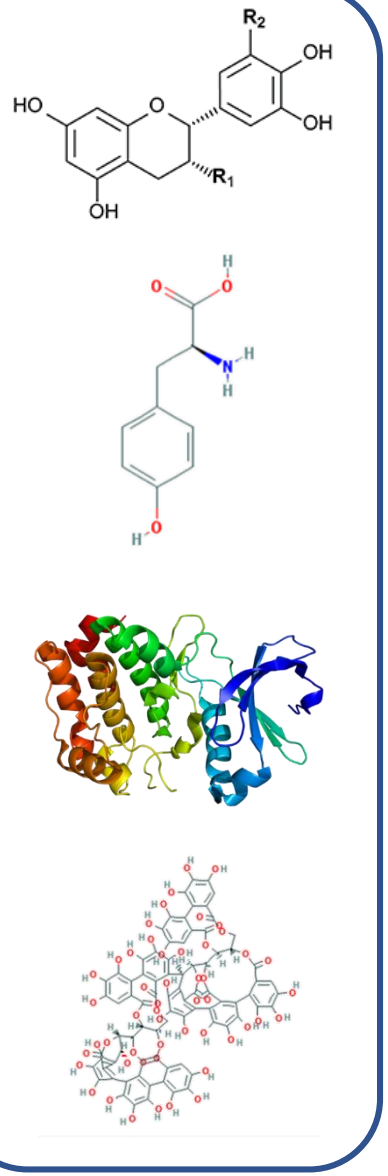


Loading fingerprints



Database

Potential wine fluorophores families



Fluorescence Fingerprinting of Bottled White Wines Can Reveal Memories Related to Sulfur Dioxide Treatments of the Must

Christian Coelho,[*,†] Alissa Aron,[†] Chloé Roullier-Gall,[†,‡,§] Michael Gonsior,[∥] Philippe Schmitt-Kopplin,[‡,§] and Régis D. Gougeon[†]

[†]UMR PAM Université de Bourgogne/AgroSupDijon, Institut Universitaire de la Vigne et du Vin, Jules Guyot, Dijon, France
[‡]Research Unit Analytical BioGeoChemistry, Department of Environmental Sciences, Helmholtz Zentrum München, Ingolstaedter Landstrasse 1, 85764 Neuherberg, Germany
[§]Chair of Analytical Food Chemistry, Technische Universität München, Alte Akademie 10, 85354 Freising-Weihenstephan, Germany
[∥]University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Solomons, Maryland 20688, United States

Challenge 1: the optimal number of component F

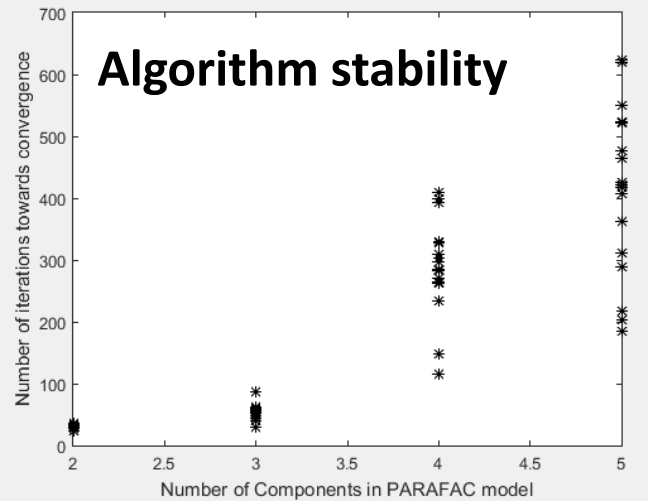
Random initialization
20 Replicates for NBC 1 -> 10

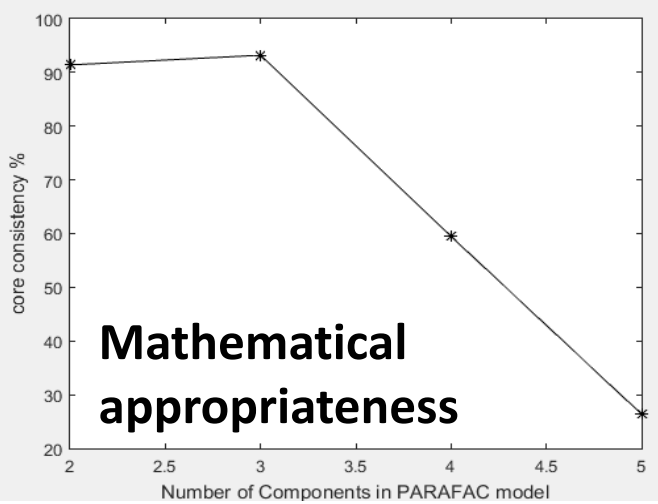
Best model selected for each NBC

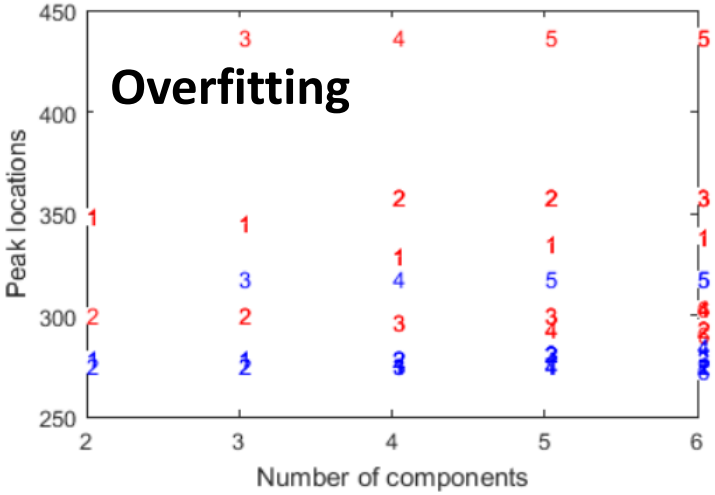
Core consistency plot

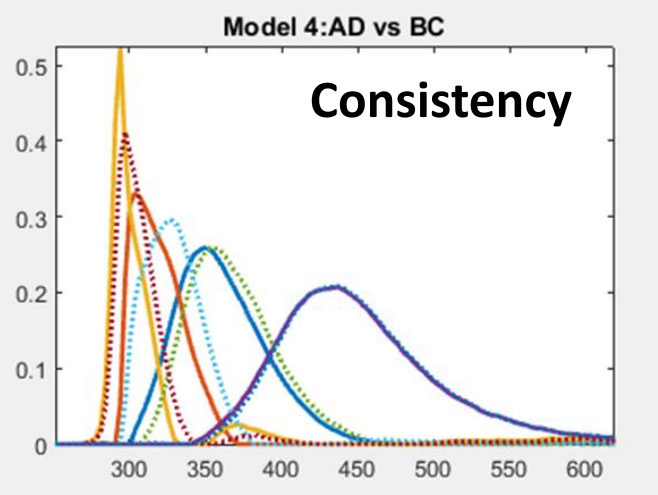
Overfitting diagonosis

Split-half validation



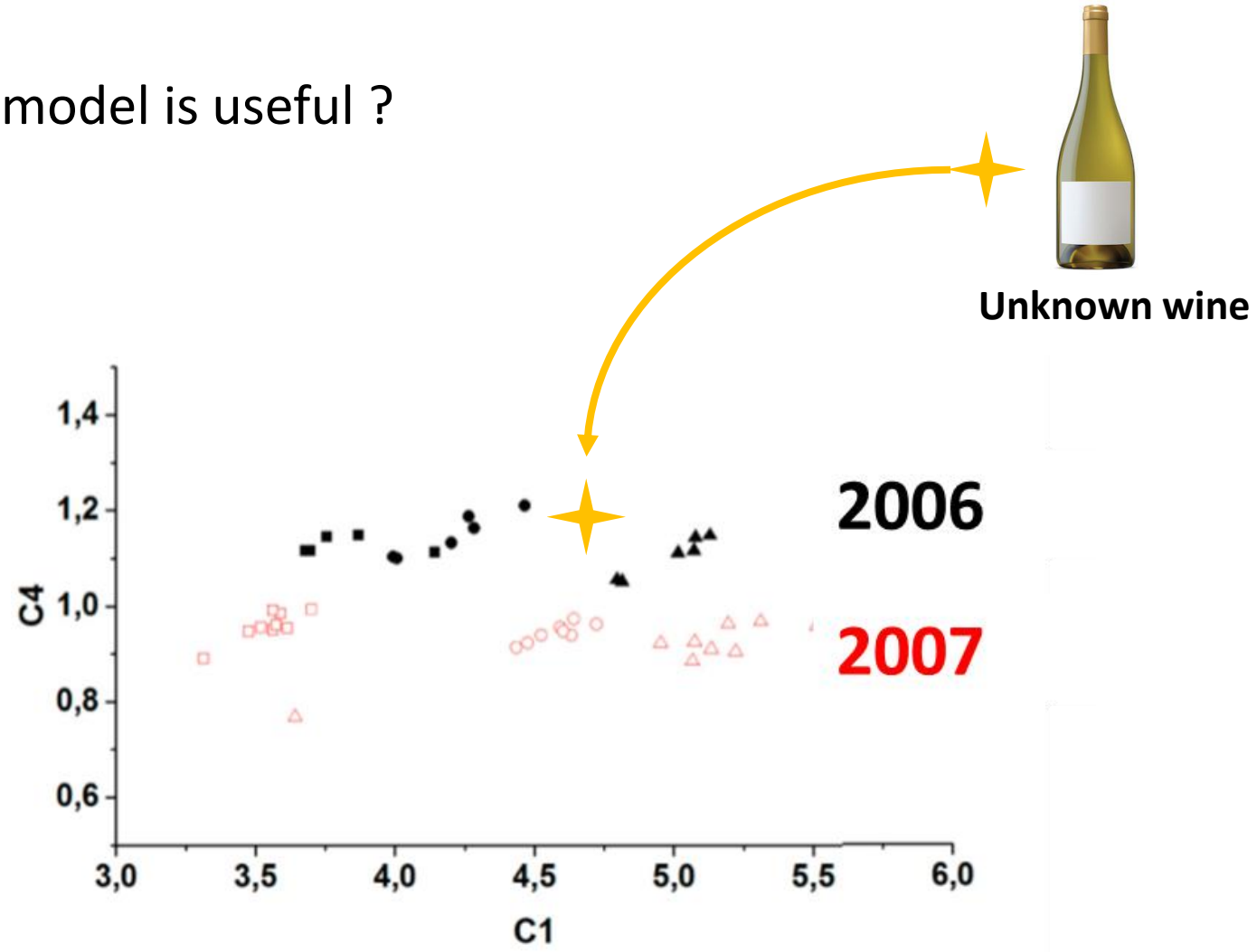






Challenge 2: towards a universal wine model

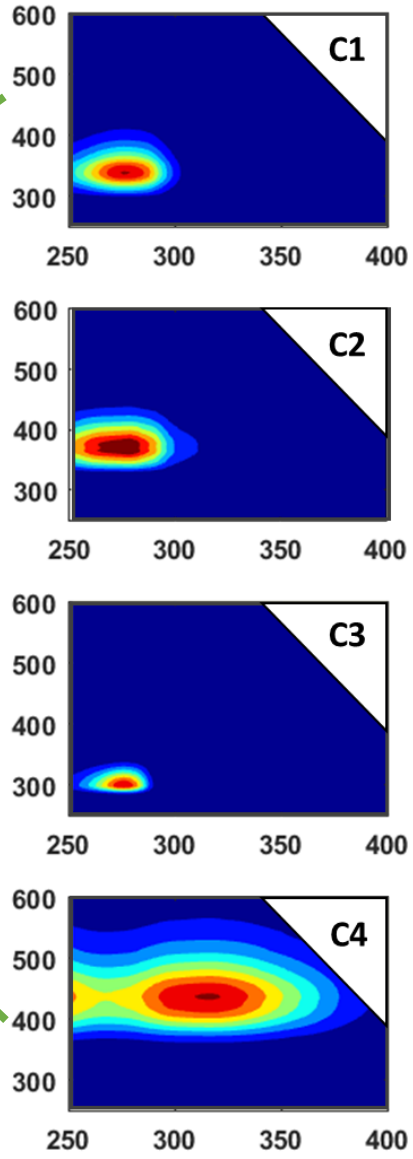
Why a universal PARAFAC model is useful ?



Challenge 2: towards a universal wine model

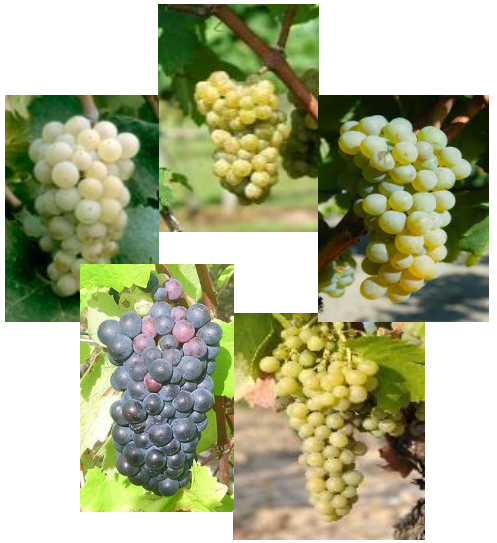
Chardonnay

(320 Wines)

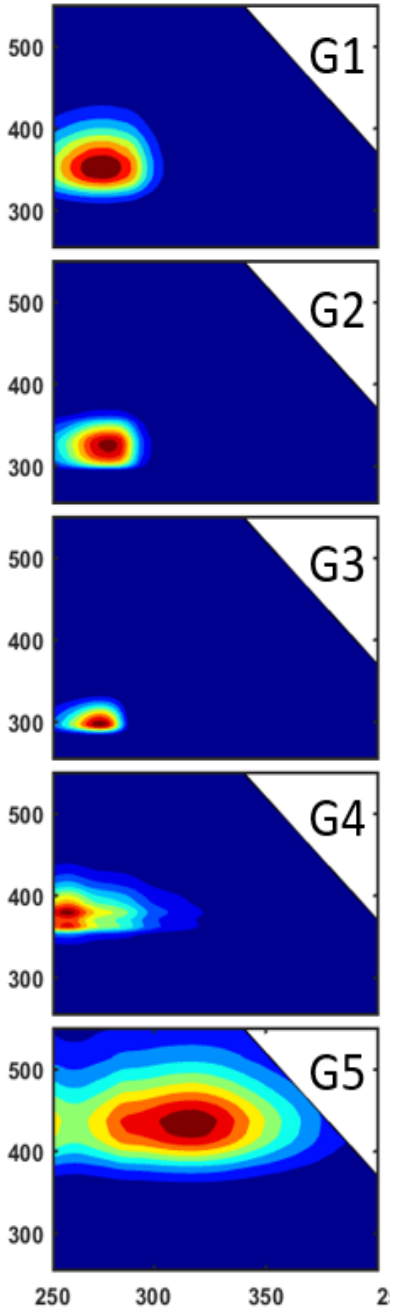


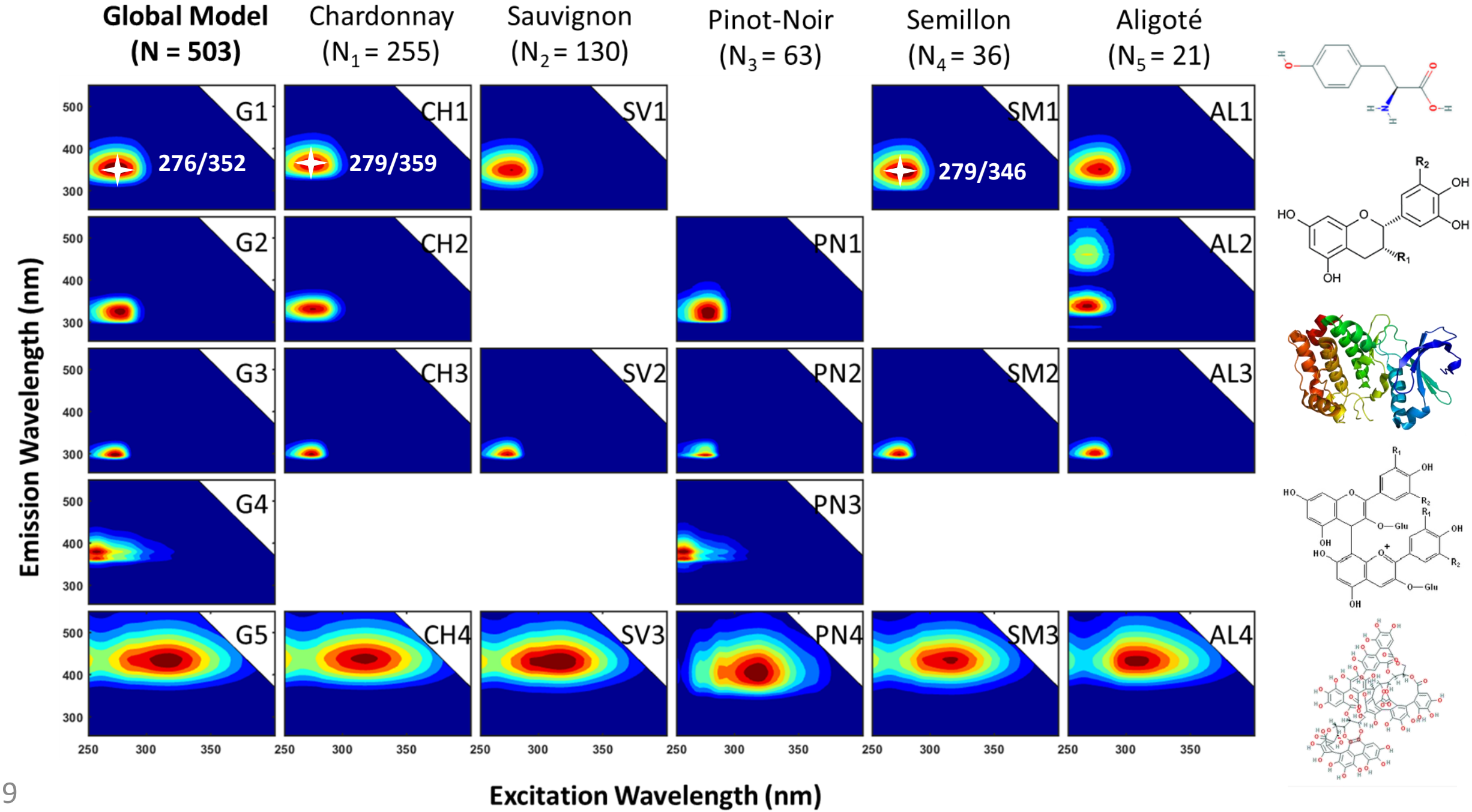
Coelho *et al.* (2015)

5 grape varieties

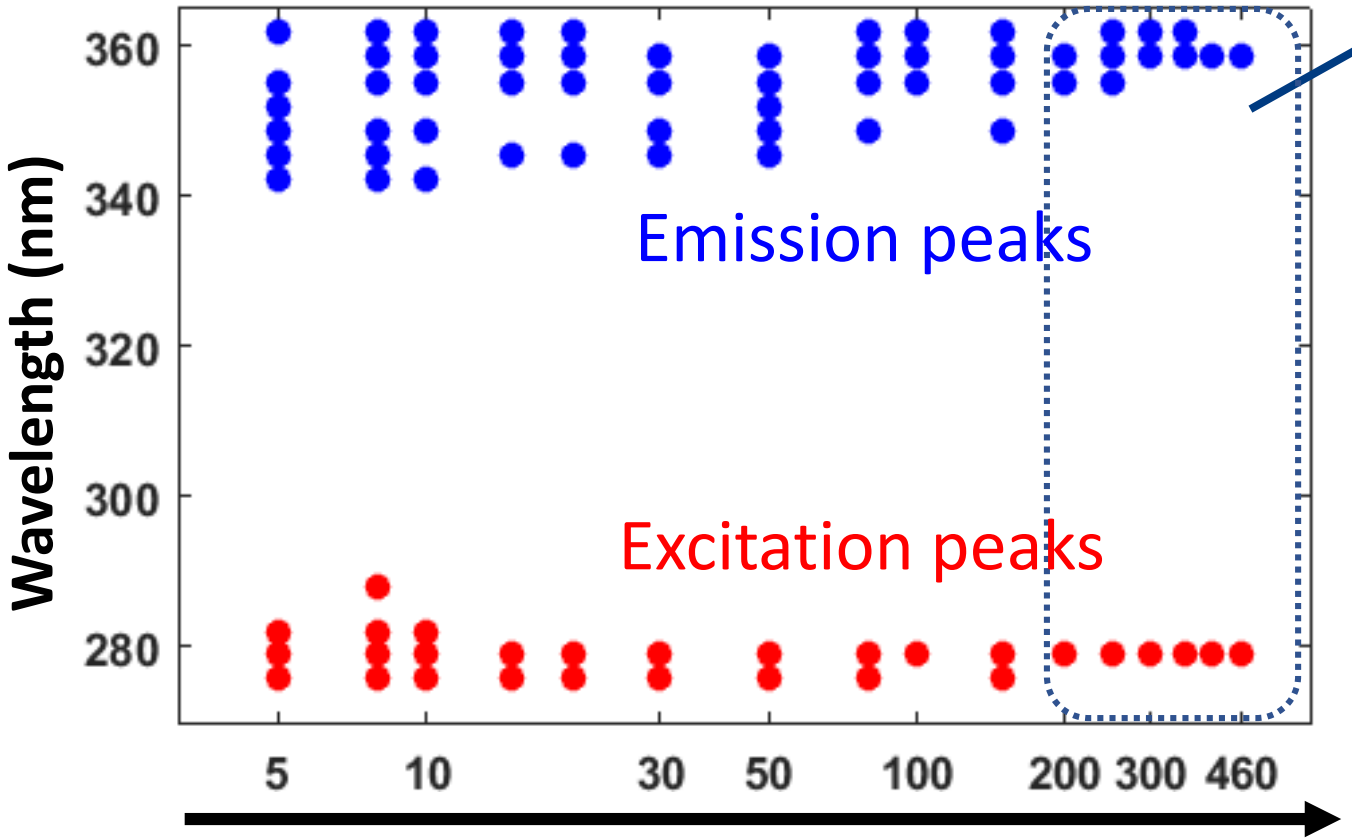


(505 Wines)

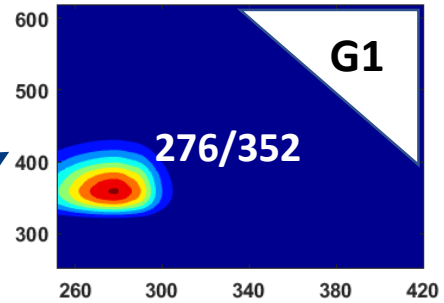



Global Model
(N = 503)
Chardonnay
(N1 = 255)
Sauvignon
(N2 = 130)
Pinot-Noir
(N3 = 63)
Semillon
(N4 = 36)
Aligoté
(N5 = 21)
G1
276/352
CH1
279/359
SV1
SM1
279/346
AL1
G2
CH2
PN1
AL2
G3
CH3
SV2
PN2
SM2
AL3
G4
PN3
G5
CH4
SV3
PN4
SM3
AL4
Emission Wavelength (nm)
Excitation Wavelength (nm)
500
400
300
250
300
350
Glu
OH
HO

Effect of sample size on PARAFAC components



Random subset of samples with increasing size



From 200 samples on, the peak location of G1 did not change any more when new samples were added

Effect of sample diversity on PARAFAC components

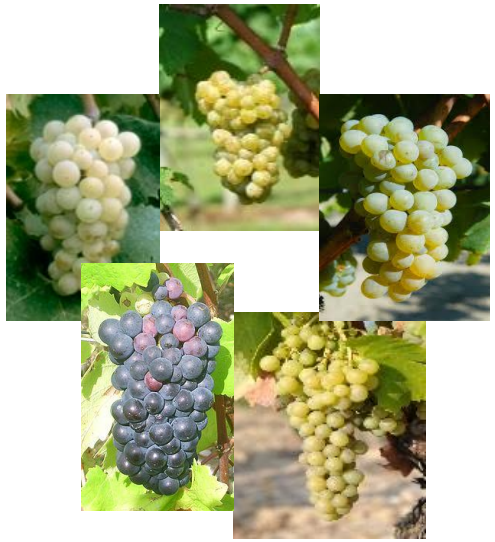
Chardonnay

250 samples

Transition models

Increasing diversity

5 grape varieties



250 samples

Take-home messages

- Wine: a complex biological matrix → complex data
- PARAFAC: higher-order PCA to interpret “photo-album” of EEMF data.
- Scores Fluorophore contents show separation between wines of diverse origins, elaboration methods…
- Loadings Translate statistical components to families of fluorophores
- PARAFAC: towards a universal wine model
- Useful for characterization of wines of any type
- Requires decent model validation workflow
- Sample size and diversity can influence the quality of universal model

Thank you for your attention !