Varietal discrimination of Extra Virgin Olive Oils – “terroir” effect

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4€/L

vs

20€/L

Quality

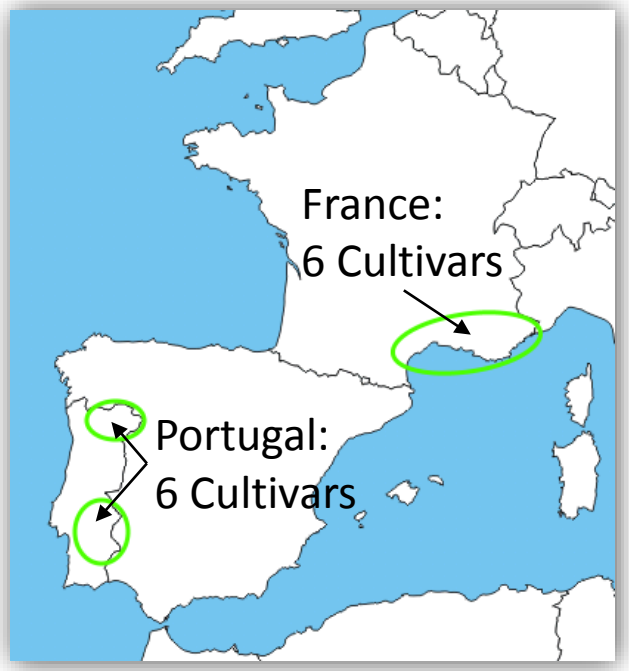
Traceability

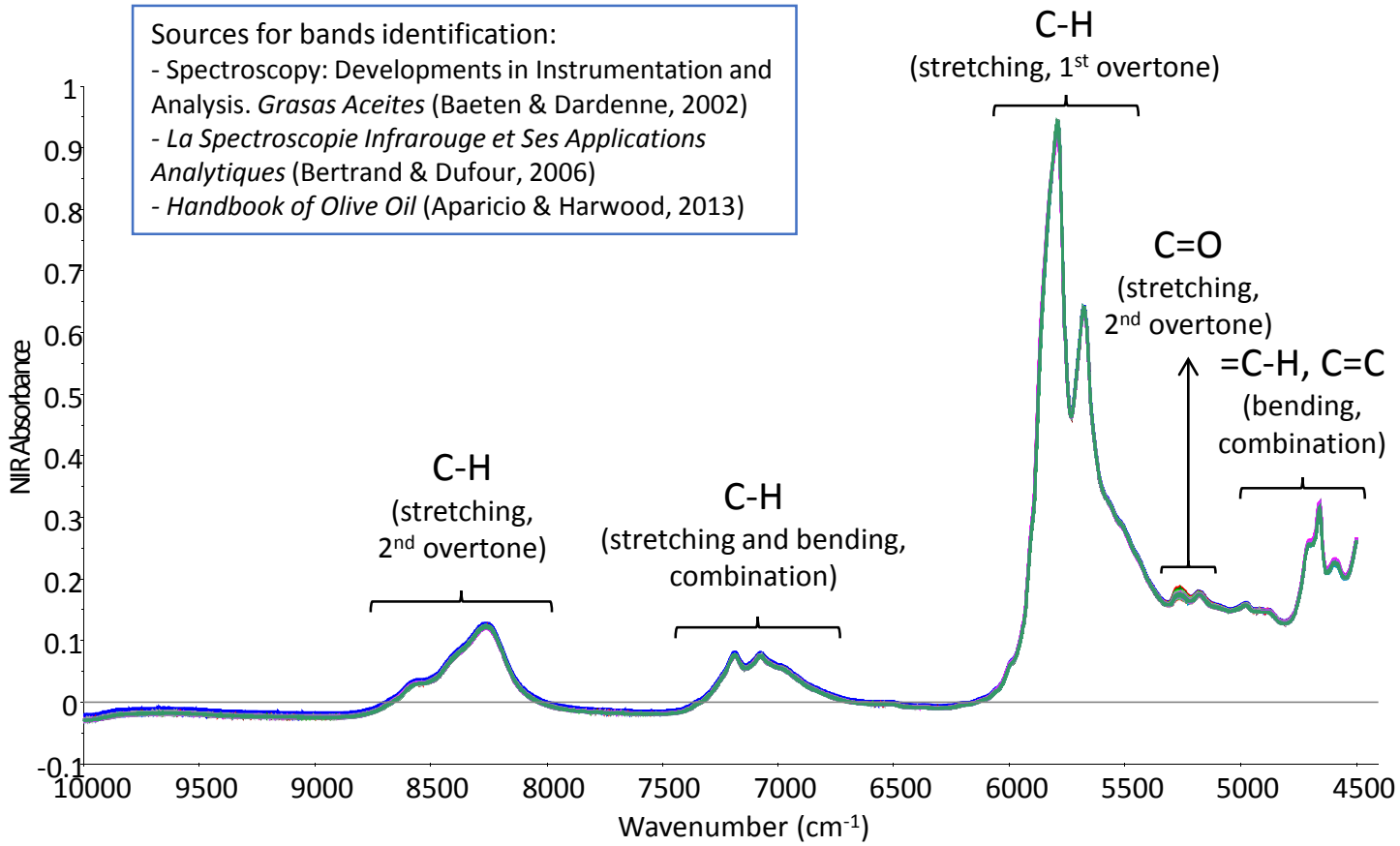
Olive variety / ripeness

Climate / soil

Agricultural practice

Extraction method

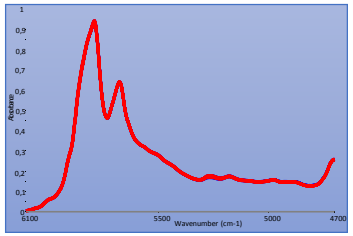




- 133 EVOO samples, 1 production year
- Near Infrared Spectroscopy: Thermo Nicolet Antaris II, 2 spectra / sample, transmission acquisition: range 10 000 to 4 500 cm^{-1}, resolution 4 cm^{-1}, accumulation 16 scans
- Chemometrics: The Unscrambler X 10.4, various pre-treatments (Detrend, SNV, SG 1st derivative, EMSC), Principal Component Analysis, Partial Least Squares 1 - Discriminant Analysis regression model

EVOO: Extra Virgin Olive Oil – SNV: Standard Normal Variates – SG: Savitzky-Golay – EMSC: Extended Multiplicative Scatter Correction

Source for PLS algorithm breakdown: CheMOOCs - Grain 8: Regression PLS, Douglas Rutledge



X = Scores × Loadings + Residuals

$$X = T \times P^T + E$$

Correlation (W)

Y

1 0 0 0
0 0 1 0
0 1 0 0
0 0 0 1

$$Y = U \times R^T + F$$

$$Y_{predicted} = X\,W\,(P^T\,W)^{-1}\,R^T$$

Samples with theoretical value = 1

- True positive if $Y_{pred} > 0.6$
- False negative if $Y_{pred} < 0.5$
- Uncertain if $Y_{pred} \in [0.5 ; 0.6]$

Samples with theoretical value = 0

- True negative if $Y_{pred} < 0.4$
- False positive if $Y_{pred} > 0.5$
- Uncertain if $Y_{pred} \in [0.4 ; 0.5]$

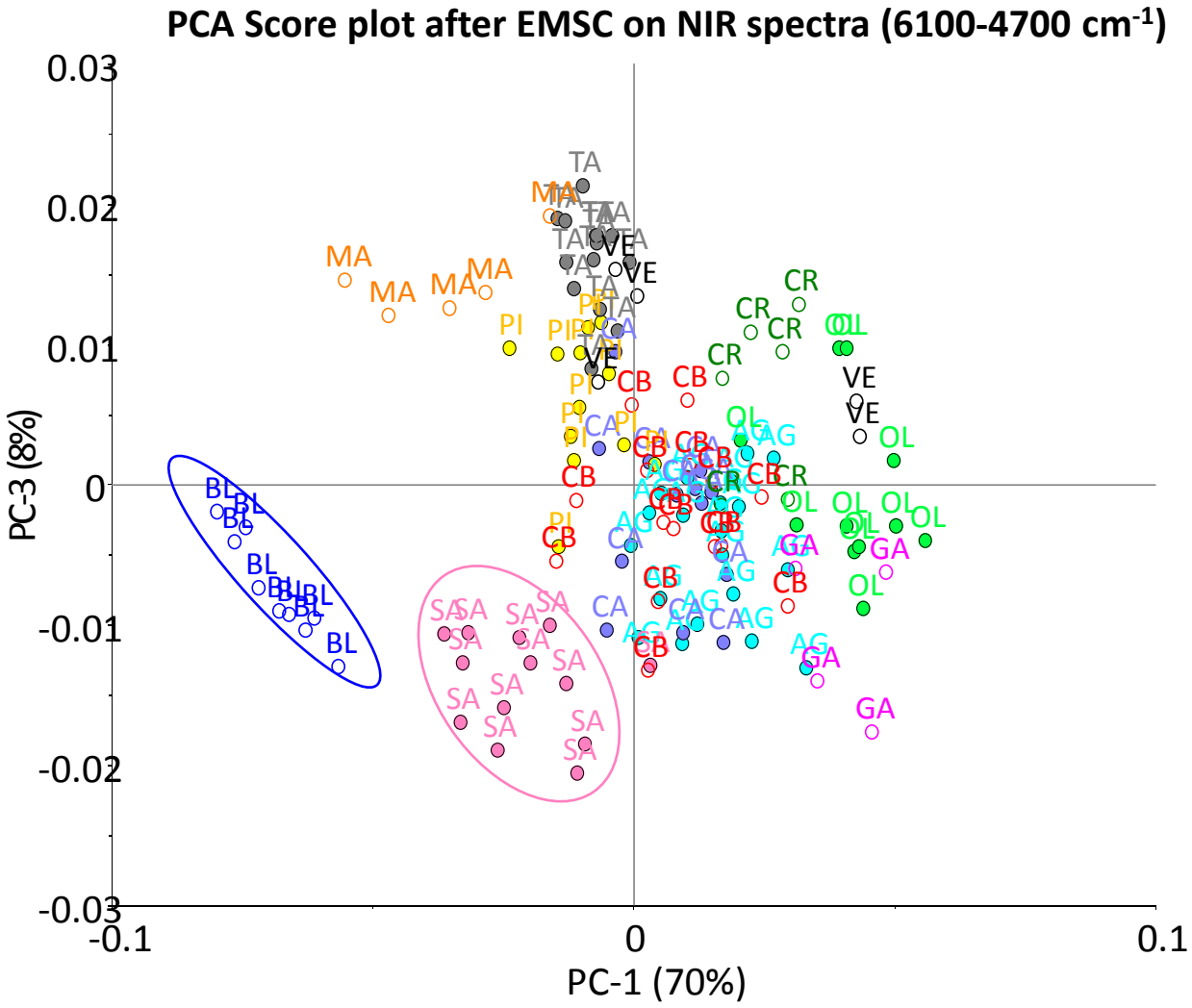
Quality criteria of the model :

$$\%\ correct = \frac{true\ positive + true\ negative}{true\ positive + true\ negative + false\ positive + false\ negative + uncertain} \times 100$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(Y_{Reference} - Y_{Predicted})^2}{n}}$$

$$sensitivity = \frac{true\ positive}{expected\ positive}$$

$$specificity = \frac{true\ negative}{expected\ negative}$$

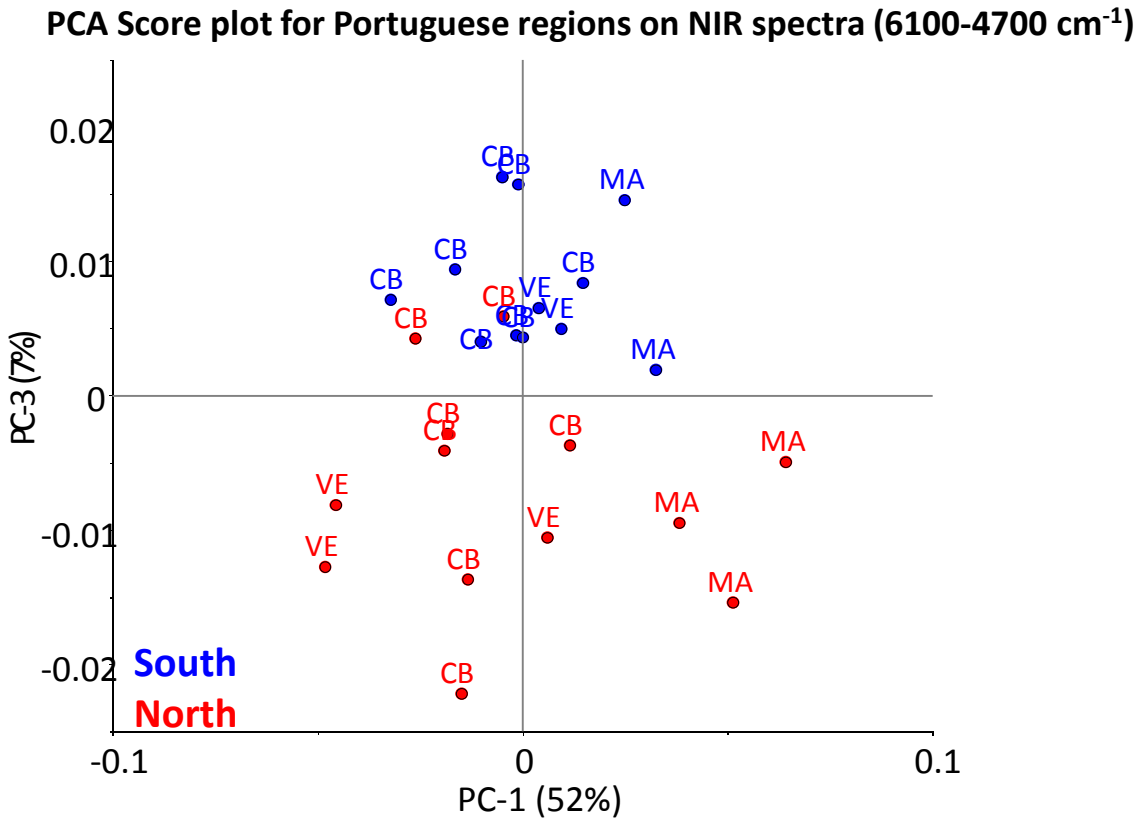


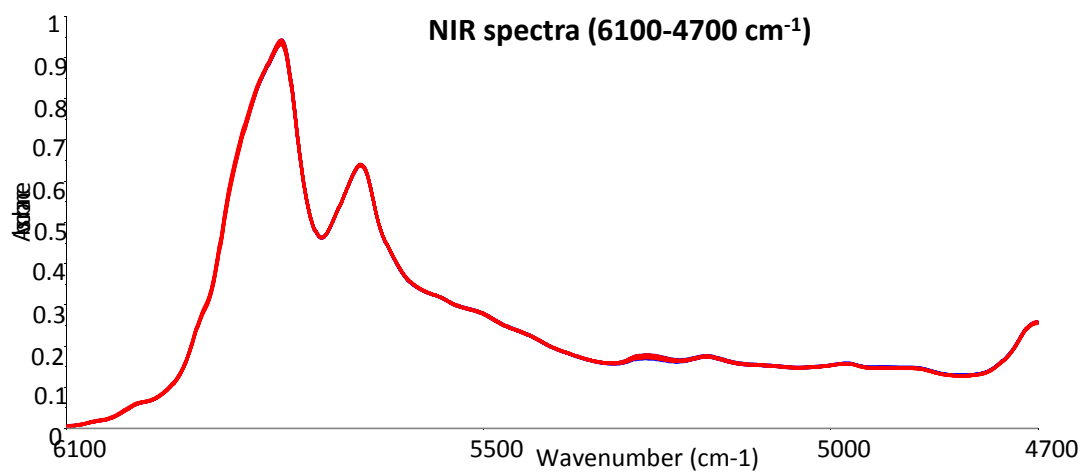
- PLS1-DA after EMSC on NIR spectra (6100-4700 cm^{-1})
- 84 samples for Calibration (C), 49 samples for Prediction (P)
- RMSEP: 0.11 to 0.32, 6 to 9 factors

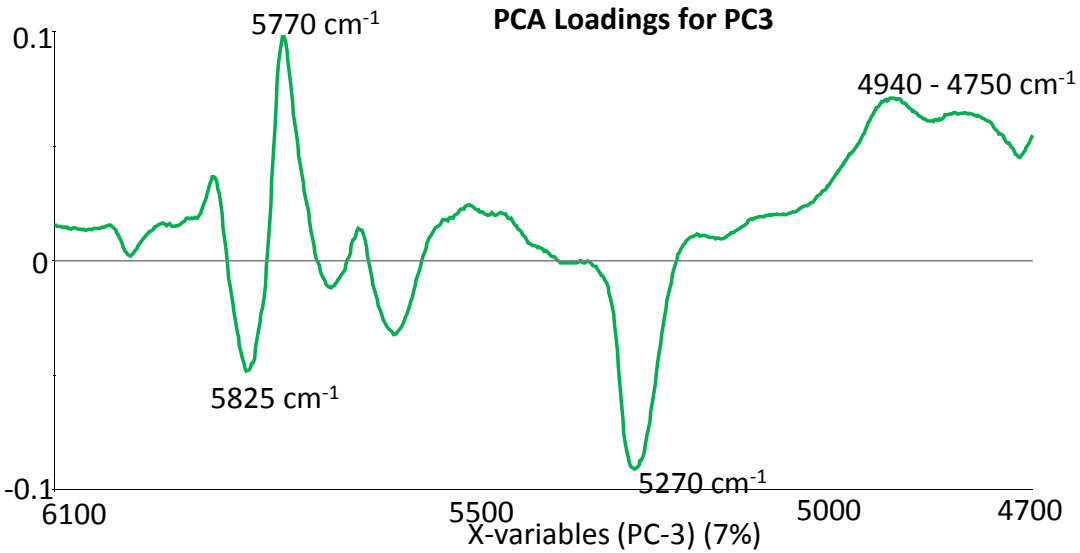
PLS1-DA Model	% Correct	% Uncertain	Sensitivity	Specificity
BL (C: 6, P; 3)	100.0%	0.0%	100.0%	100.0%
OL (C: 8, P: 4)	98.0%	2.0%	100.0%	97.8%
TA (C: 10, P: 5)	98.0%	2.0%	80.0%	100.0%
SA (C: 8, P; 6)	93.9%	2.0%	66.7%	97.7%
AG (C: 14, P: 7)	91.8%	0.0%	100.0%	90.5%
CA (C: 9, P: 5)	89.8%	4.1%	20.0%	97.7%
PI (C: 8, P: 5)	87.8%	2.0%	0.0%	97.7%
CB (C: 9, P: 6)	85.7%	8.2%	33.3%	93.0%
CR (C: 4, P: 2)				
GA (C: 2, P: 2)				
MA (C: 3, P: 2)				
VE (C: 3, P: 2)				
Average	**93.1%**	**2.6%**	**62.5%**	**96.8%**

- French Cultivars: AG (Aglandau), CA (Cailletier), OL (Olivière), PI (Picholine), SA (Salonenque), TA (Tanche)
- Portuguese Cultivars: BL (Blanqueta), CB (Cobrançosa), CR (Cordovil), GA (Galega), MA (Madural), VE (Verdeal)

Results : Varietal discrimination







PLS1-DA Model	% Correct	% Uncertain	Sensitivity	Specificity	Factors	RMSEP
North vs South (C: 16, P: 9)	88.9%	11.1%	80.0%	100.0%	3	0.23

Conclusion and perspectives:

- Possible discrimination of EVOO samples depending on Cultivars and Region of origin : “terroir” effect?
- More samples to be analysed / several other analytical techniques / chemometrics on concatenated data