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NIR PLS prediction of quality parameters of olive oils at different stage of ageing

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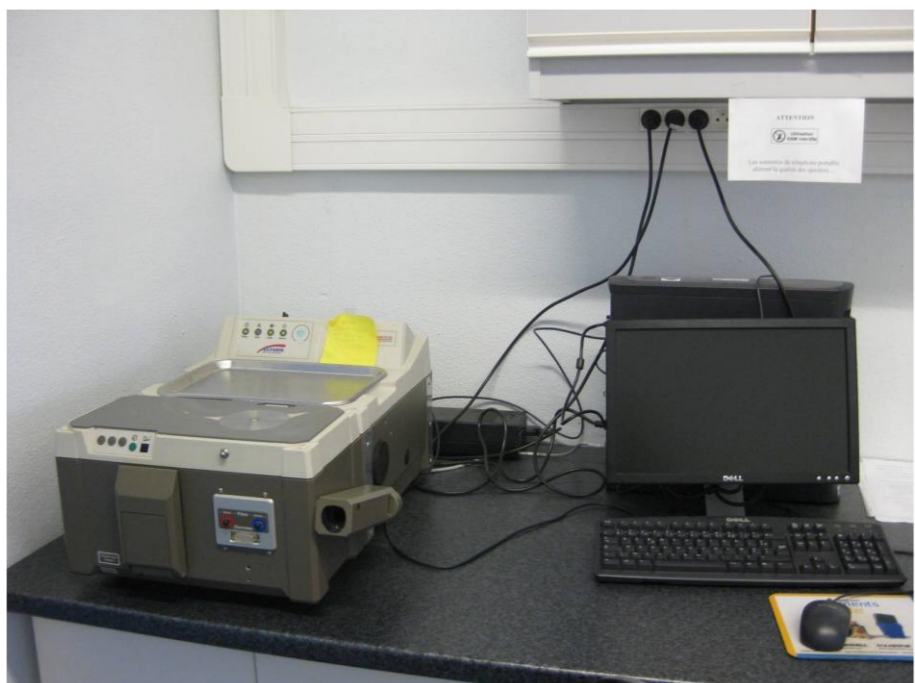
Introduction

The oils are foods essential to our health because they contain some fatty acids not synthesized by the human body. Deterioration is due to oxidation (rancidity) that reduces the shelf life and nutritional value of some compounds and, moreover, generates toxic products. The olive oil quality may be affected at different stages of processing, bottling and storage. Then, several parameters are usually measured: peroxide value (PV), anisidine value (AV), Totox value (TOTOX), free acidity (FA), spectroscopic indexes (K232 and K270), fatty acid composition and total phenols content (PT) according to norms, but required time-consuming analytical procedures. NIR measurements have been successfully used for their determination from partial least squares regression (PLS) models in the case of fresh oils. The present work investigates this methodology for two olive oils (green and black fruity) aged under different temperature (variable (Tv) or fixed (Tf), light (darkness (N), direct (UV) or indirect light (L)), presence of oxygen (renewed (O) or not) and storage time (0-20 months) conditions.

Analytical methodology

FT-NIR analysis

Samples were measured in glass tubes of 4 mm diameter



Spectral range: 10000 à 4500 cm^{-1}
Resolution : 4 cm^{-1}
Accumulation: 16 scans
Background on empty tube
Software: Result TM V2.0 of Thermo Scientific

PLS model

Wavenumbers → Analysis Data

FT-NIR data

PV
AV
TOTOX
FA
PT
K232
K270

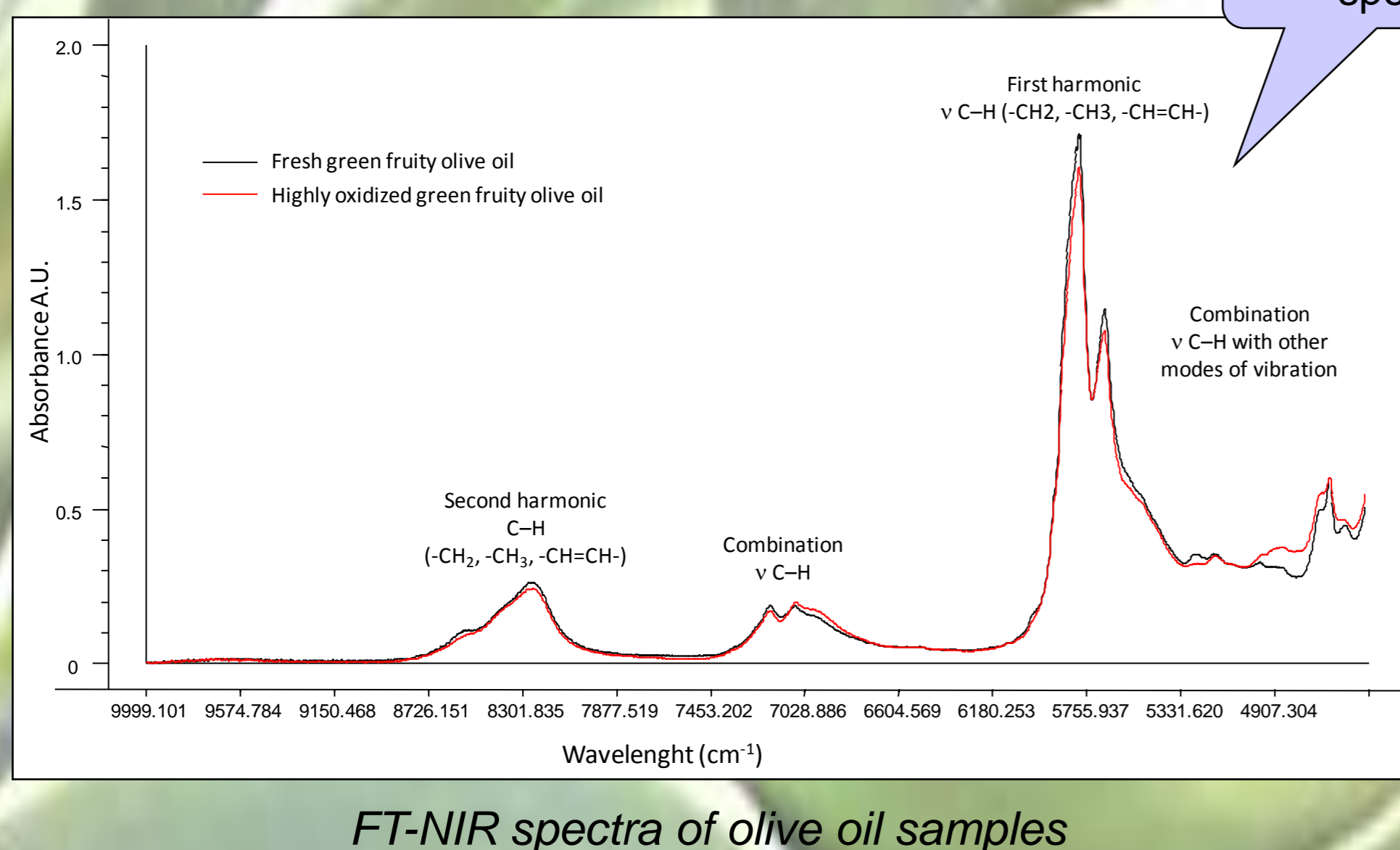
0 < PV (meq $\text{O}_2 \cdot \text{kg}^{-1}$) < 104
2.2 < AV < 10.8
2.5 < TOTOX < 215.1
0.25 < FA (%oleic acid) < 1.43
2.2 < K232 < 8.0
0.15 < K270 < 0.33
76.7 < PT (mg.kg $^{-1}$) < 550.8

Reference data

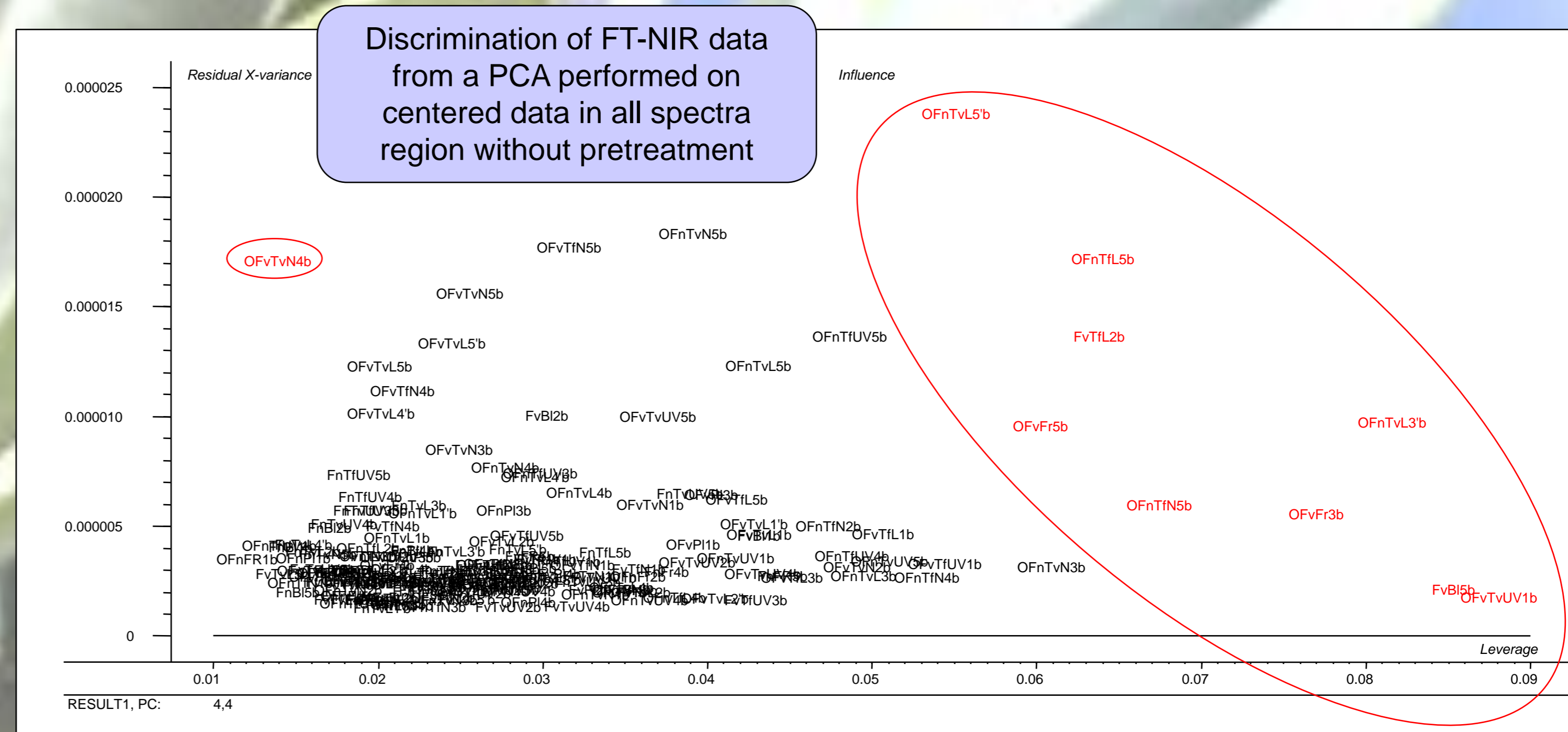
- PV from ISO 3960 method (2007)
- AV from ISO TC34/SC 11 method (2003)
- TOTOX from works of Poulli et al. method (2009) ; TOTOX = 2 PV + AV
- FA from ISO 660 method (2009)
- K232 and K270 from International Olive Council method (2010)
- PT from works of Singleton et al. method (1999)

Analysis of 190 samples aged during 4 to 20 months

Results



Similarity of oil spectra



Spectral residuals variances of samples used for models (black) and outliers (red)

To predict quality parameters, two PLS models were built with a permutation of samples between calibration and prediction sets using 120 samples randomly selected for the calibration set and 60 remaining for the prediction set. After a standard normal variate (SNV) and baseline corrections as pretreatments, a cross-validation was realized on selected spectral range (from 7158 to 5875 and 5332 to 4499 cm^{-1}) to choose the optimal number of latent variables.

Results for the first model

Predicted quality parameter	Min value	Max value	Calibration (n=120)		Validation (p=60)		
			SEC	R ²	SEP	R ²	LV
PV	0.00	104.03	3.17	0.99	4.09	0.97	7
AV	2.20	10.76	0.78	0.94	1.17	0.86	7
TOTOX	2.51	215.09	6.12	0.99	7.83	0.97	7
FA	0.25	1.43	0.05	0.99	0.09	0.97	7
Total phenols	76.73	550.78	47.52	0.94	62.53	0.88	6
K232	2.20	7.99	0.25	0.96	0.41	0.85	7
K270	0.15	0.33	0.03	0.75	0.03	0.51	4

SEC : standard error of calibration
SEP : standard error of prediction
R² : correlation coefficient
LV : number of latent variables

Results for the second model

Predicted quality parameter	Min value	Max value	Calibration (n=120)		Validation (p=60)		
			SEC	R ²	SEP	R ²	LV
PV	0.00	104.03	3.16	0.99	3,80	0,97	7
AV	2.20	10.76	0.54	0.97	1,05	0,88	8
TOTOX	2.51	215.09	6.14	0.99	7,59	0,97	7
FA	0.25	1.43	0.06	0.99	0,07	0,98	7
Total phenols	76.73	550.78	40.11	0.96	58,40	0,91	7
K232	2.20	7.99	0.48	0.87	0,27	0,93	5
K270	0.15	0.33	0.03	0.76	0,03	0,57	6

The results from two sample sets are relatively closed, which confirms the quality of the models. Except for the models for K270, all models provide satisfactory prediction results (validation R² > 0.85). Thus, the quality parameters of a sample can be determined from its near infrared spectrum, which represents a time saving. As the SEP values were smaller than twice the SEC values, it suggests that there is no over-fitting, although the relatively high number of latent variables (4-8). The models for K270 provided unsatisfactory results (validation R² = 0.51 and 0.57). However, that is explained by the fact that this parameter changed weakly during ageing.

Conclusion

PLS models based on FT-NIR data have demonstrated that it was possible to quickly determine the main quality parameters of olive oil and thus saving time and chemical products compared to conventional methods. However, because of the low variability of K270 parameter, no reliable model could have been established. It would be interesting to expand the database with samples having very different K270 levels, which will also permit to consolidate models. Moreover models quality was proved because the permutation samples for calibration and validation has permit to built very closed models.

References

- ISO 3960. (2007). Animal and vegetable fats and oils - Determination of peroxide value.
- ISO 660. (2009). Animal and vegetable fats and oils - Determination of acid value and acidity.
- ISO TC34/SC 11. (2003). Animal and vegetable fats and oils - Determination of anisidine value.
- International Olive Council. (2010). Spectrophotometric investigation in the ultraviolet, T.20 (Doc n°.19).
- Poulli, K. I., Mousdis, G. A., & Georgiou, C. A. (2009). Monitoring olive oil oxidation under thermal and UV stress through synchronous fluorescence spectroscopy and classical assays. *Food Chemistry*, 117(3), 499-503.
- Singleton V. L., Orthofer R & Lamuela-Raventos R. M., (1999) Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. *Methods in Enzymology*, 299, 152-178.