Green and fast determination of ethyl ester content in olive oil by IR spectroscopy

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According to the Regulation (EU) 2016/2095, extra virgin olive oils must contain a maximum of 35 mg/kg of fatty acid ethyl esters (FAEE). However, the official method for FAEE quantification requires the use of toxic solvents and is time-consuming. Thus, the aim of this work was the application of FT-IR and FT-NIR spectroscopy for the development of partial least squares (PLS) models predicting FAEE content in olive oils. Spectra of 197 olive oil samples with known FAEE content (0.92-111.63 mg/kg) were collected in duplicate in the ranges 4000-700 cm^{-1} (FT-IR) and 12500-4000 cm^{-1} (FT-NIR), with 8 cm^{-1} resolution and 16 scans for both samples and background. Before elaborations, the noisy and less informative spectral regions were eliminated and the reduced spectra were averaged and pre-treated with different algorithms (i.e., smoothing, standard normal variate, and first derivative, alone or in combination). First, an exploratory principal component analysis (PCA) was carried out, which enabled the elimination of few outliers. Then, the Kennard Stone algorithm was applied to partition the whole datasets in calibration (70% samples) and validation (30% samples) sets. PLS models were developed for the two spectral ranges separately, considering both the whole FAEE content range and a reduced range (0.92-50 mg/kg). All the developed models were validated internally (cross-validation) and externally (validation set), and predicting performances were evaluated in terms of coefficients of determination (R^2_{pred}) and root mean square errors (RMSEP). The best models were obtained considering the reduced range of FAEE concentration, with R^2_{pred} of 0.85 and 0.63 for FT-NIR and FT-IR spectroscopy, respectively, and reasonably small values of RMSEP (4.63 and 6.61 mg/kg respectively for FT-NIR and FT-IR ranges). Thus, IR spectroscopy, especially in the NIR range, showed great potential in the development of green and fast methods for FAEE determination in olive oils and further investigations are encouraged to make the developed models more precise and robust.

Acknowledgements: This work was supported by AGER 2 Project, grant no. 2016-0105. A special thanks to Ece İnceoğlu and Daniela Cela for their help in the analyses.