NIR spectroscopy for examining environmental parameters affecting olive oil quality and for quantifying adulterations of extra virgin olive oil with low grade edible oils

N. Heigl, C.H. Petter, G.K. Bonn and C.W. Huck*

Institute of Analytical Chemistry and Radiochemistry, Leopold-Franzens University, Innrain 52a, 6020 Innsbruck, Austria. E-mail: christian.w.huck@uibk.ac.at

Introduction

Near-infrared (NIR) spectroscopy has been recognised as a powerful analytical tool for quantifying adulterations of pure extra virgin olive oil by addition of sunflower, soya, rape, safflower and hot-pressed olive oil. The NIR spectral region (4000–12800 cm^{-1}) covers overtones and combination bands of fundamentals that arise in the mid-infrared (400–4000 cm^{-1}), while NIR spectroscopy comprises a non-invasive, non-destructive and low-cost technique presenting a simple and flexible working environment,[1,2] being highly suitable for olive oil analysis.[3–12] The aim of this study was to determine the role of NIR in predicting the amount of cheap adulterants in the rather expensive, high quality olive oil in a first approach. A second aspect of the work was to determine the influence of the choice of glass of bottles used for storage on the NIR application, concerning the prediction of acid number, peroxide and iodine values.

Materials and methods

NIR spectra were recorded with a scanning polarisation interferometer Fourier-transform NIR spectrometer (FT-NIR) (Büchi, Flawil, Switzerland). The FT-NIR instrument offers a resolution of 12 cm^{-1}, an absolute wavelength accuracy of $\pm$ 2 cm^{-1} and a relative reproducibility of 0.5 cm^{-1}. Chemometric software NIRCal 4.21 (Büchi) was used for creating the principal component analysis (PCA) and partial least squares (PLS) regression models. For testing the models the collected spectra were divided into a learning-set (c-Set, 67%) and a test-set (v-Set, 33%) both consisting of independent samples. Measurements were carried out at room temperature (23°C) from 4000 to 10000 cm^{-1}.

Results and discussion

Recorded spectra of the olive oil mixtures, containing varying adulterants in a range from 0–100 %, were subjected to adjacent multivariate calibration, such as partial least squares regression (PLSR) and principal component regression (PCR) for estimating the amount of adulteration by means of NIR spectroscopy. Quantitative models established in this overall study enabled the prediction of the amount of added adulterants in high quality olive oils with a standard error of prediction (*SEP*) of minimum 2.62% and maximum of 5.36% between 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 and 100% (Figure 1).

Furthermore, principal component analysis (PCA) enabled creating 2- and 3-dimensional cluster models that show clearly the classification and differentiation of differing types of edible oils, based on its associated loading values (Figure 2).

Moreover, a setup was established called “the roof experiment”. In this experiment *extra virgin* olive oil was poured into four different vessels varying in material (glass, aluminium) and colour (white, green, brown glass). Every bottle was put under extreme conditions (high temperature, sunlight, rain etc.) on a roof (Figure 3) to get information upon changes into the olive oil composition.

Periodical NIR measurements were carried out after 4, 9 and 16 weeks, with the objective of establishing calibration models based on reference values (gas-chromatography mass-spectrometry (GC-MS) and titration methods) for further predictions of acid number, peroxide and iodine values that change with duration of the experiment, and to follow these changes via NIRS. It was

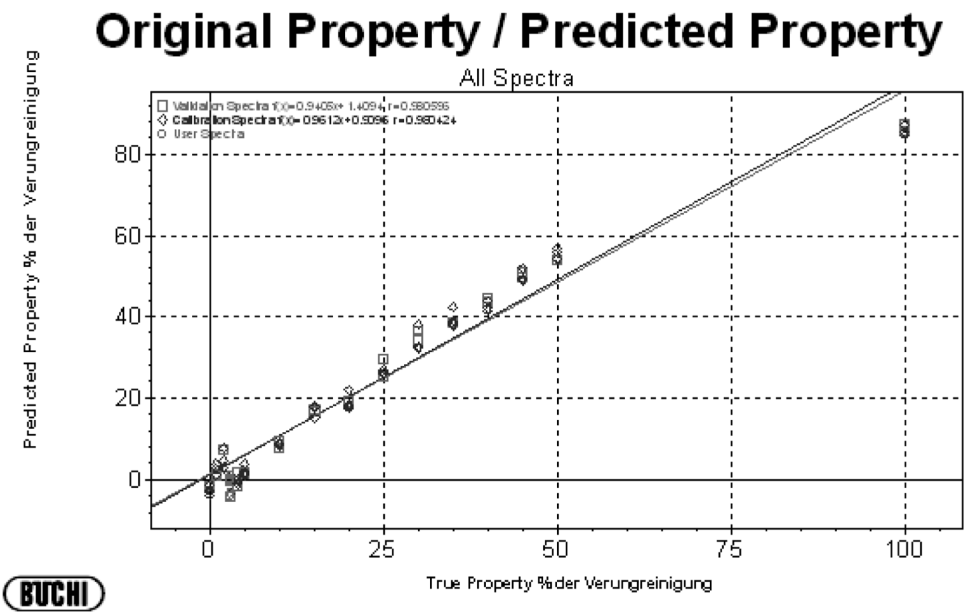

Figure 1. Partial least squares regression (PLSR) for estimating the amount of adulteration by means of NIR spectroscopy.

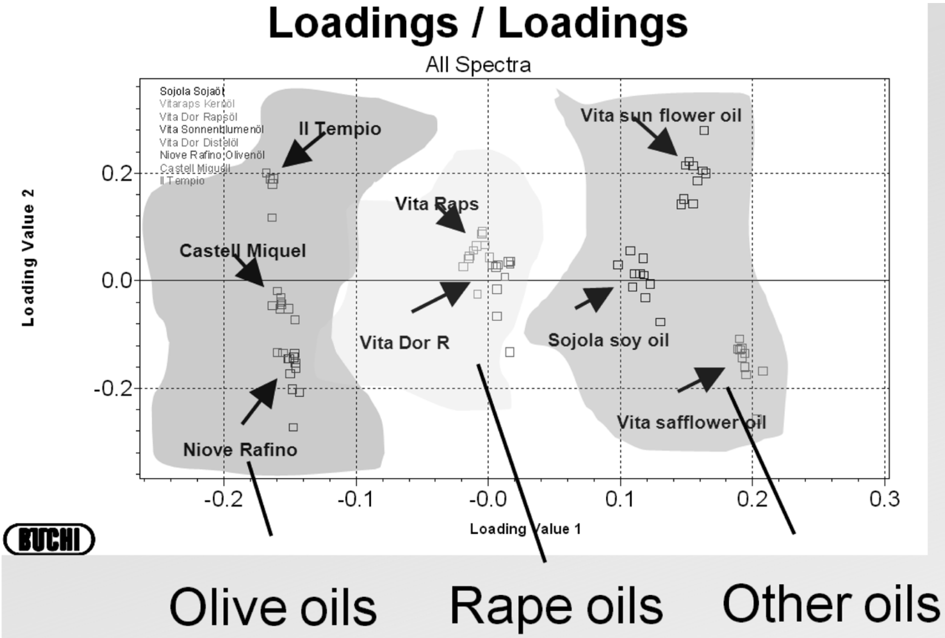

Figure 2. 2-dimensional factor plot for the classification and differentiation of differing types of edible oils based on associated loading values.

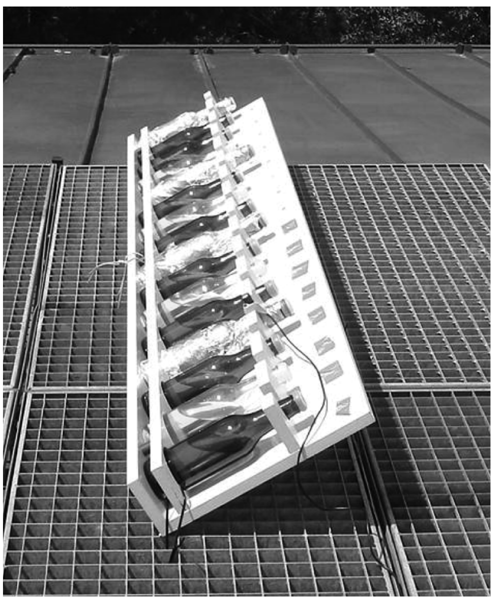

Figure 3. Experimental setup for the "roof experiment".

Table 1. Calibration parameters for the determination of the acid number, peroxide and iodine values in brown glass bottled extra vergin olive oil.

Q-Value	0.923002		
	Peroxide number	Iodine number	Acid number
C-Set BIAS	7.32E-14	–4.54E-16	–1.03E-17
V-Set BIAS	–0.0367216	–0.000146467	–0.000119456
C-Set SEE	0.742888	0.00539997	0.00187004
V-Set SEE (SEP)	0.784202	0.00435723	0.00152942
Consistency	94.7317	123.931	122.271
C-Set Regression Coefficient	0.999873	0.995428	0.998381
V-Set Regression Coefficient	0.999906	0.997473	0.999165
C-Set Regression Intercept	0.0150431	0.00342422	0.00139481
V-Set Regression Intercept	0.603952	0.00829368	0.00284825
C-Set Regression Slope	0.999747	0.990876	0.996765
V-Set Regression Slope	0.99137	0.978762	0.993766

found that brown glass ensures the most efficient protection of olive oil. From Table 1 calibration parameters can be gathered.

The method is considered to be highly suitable to determine the acid number, peroxide and iodine values simultaneously.

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