APPLICATION OF NIR SPECTROSCOPY BY DETERMINATION OF QUALITY PROPERTIES OF VEGETABLE OILS AND THEIR DERIVATIVES

A. FÜLÖP[✉], M. KRÁR, J. HANCSÓK

Department of Hydrocarbon and Coal Processing, University of Pannonia, P. O. Box 158., H-8201 Veszprém, HUNGARY
Phone: +3688624414, Fax:+3688624520
[✉]E-mail: fulopa@almos.uni-pannon.hu

This study shows that near-infrared spectroscopy is a reliable technique to determine the concentration of the key fatty acid (FA) components (oleic, linoleic, linolenic acid), the acid number, the iodine value and the kinematic viscosity at 40 and 100 °C in sunflower and rapeseed oils. To establish the chemometric model, a calibration set of 36 rapeseed oil samples and 47 sunflower oil samples were used and 51 oil samples were used for external validation. All samples were measured on a BRUKER-MPA spectrometer in transmittance mode. The samples were scanned in a wave number range of 12000–4000 cm^{-1} with a resolution of 2 cm^{-1}. The sample scan time was 32 scans. To develop and optimize the calibration models partial least squares (PLS) method was used with cross validation.

The result of the experiment showed that this technique is sufficiently accurate for estimating the FA composition, the acid number, the iodine value and the kinematic viscosity at 40 and 100 °C in sunflower and rapeseed oil. The calibration results had root mean square error of cross validation (RMSECV) for oleic acid, linoleic acid, linolenic acid, acid number, iodine value, viscosity at 40 °C, viscosity at 100 °C of 0.395, 0.451, 0.0932, 0.208, 0.418, 0.12, 0.0237 respectively and determination coefficient (R2) (%) for the same properties of 99.96, 99.97, 99.95, 99.47, 99.88, 99.7, 99.22 respectively.

Keywords: near infrared spectroscopy, sunflower oil, rapeseed oil

Introduction

The rising population and thus, the increasing amount of motor vehicles on the world cause higher and higher fuel consumption. Besides this, the amount of the fossil fuels is decreasing in the world. That's why the research of possibilities how the use of fossil fuels can be reduced is a very important challenge nowadays. Vegetable oils and their derivatives are one of the most important sources to substitute fossil fuels. Besides, the use of vegetable oils and their derivatives as fuel reduces the amount of carbon-dioxide in the air, because the emitted carbon-dioxide will be used for photosynthesis by the growing oil plants. For that reason the determination of the quality of vegetable oils and their derivatives became important not only for the use as edible oil but also for the use as fuel.

The near-infrared spectroscopy (NIR) is a well-established analytical technique based on the absorption of electromagnetic energy in the region of 12000–4000 cm^{-1}. This type of technique allows the determination of physical and chemical properties of multi-component systems (gasoline, diesel oil, vegetable oil, etc.) in a fast and non-destructive way, without requiring complex sample pre-treatments [1-2].

In the NIR region, a component typically absorbs at more than one wavelength. On the other hand, absorbance at a given wavelength may have contributions from more than one property. Therefore, a well-established tool like partial least square (PLS) was used for the determination of the vegetable oil properties. The correlation between the absorption of NIR radiation and the analytical reference data can be improved through the use of specific spectra pre-processing methods. Pre-processing of spectra reduces variations that not directly related to the given property, such as random noise, baseline drift, etc [3-4].

In respect of using vegetable oils and their derivatives as fuel there are many significant quality properties that we have to measure such as fatty acid composition, acid number, iodine value etc. In this study we dealt with the determination of the concentration of the key fatty acid (FA) components (oleic, linoleic, linolenic acid), the acid number, the iodine value and the kinematic viscosity at 40 and 100 °C in sunflower and rapeseed oils.

Materials and methods

Oil samples

The 134 different types of rapeseed and sunflower oil samples were obtained from various locations of Hungary. The sample set was split in to two parts: 83 samples were used to establish and develop the

chemometric models and 51 samples were used for external validation.

The properties of the samples were determined by the appropriate EN ISO standard methods.

Spectra collection and data pre-treatment

To perform the NIR spectroscopic analysis a BRUKER-MPA near-infrared spectrometer was used that works with the OPUS controller software. All samples were measured in transmittance mode in a wave number range of 12000–4000 cm^{-1} with a resolution of 2 cm^{-1}. The sample scan time was 32 scans. The spectral data of the oil samples were collected as absorbance spectra. The raw NIR spectrums are shown in *Fig. 1*.

For data pre-processing two manipulation methods were applied: the base line correction and the smoothing with smoothing points of 25. The manipulated spectrums are shown in *Fig. 2*. The OPUS software applied further data treatment methods during the optimization process if it is necessary.
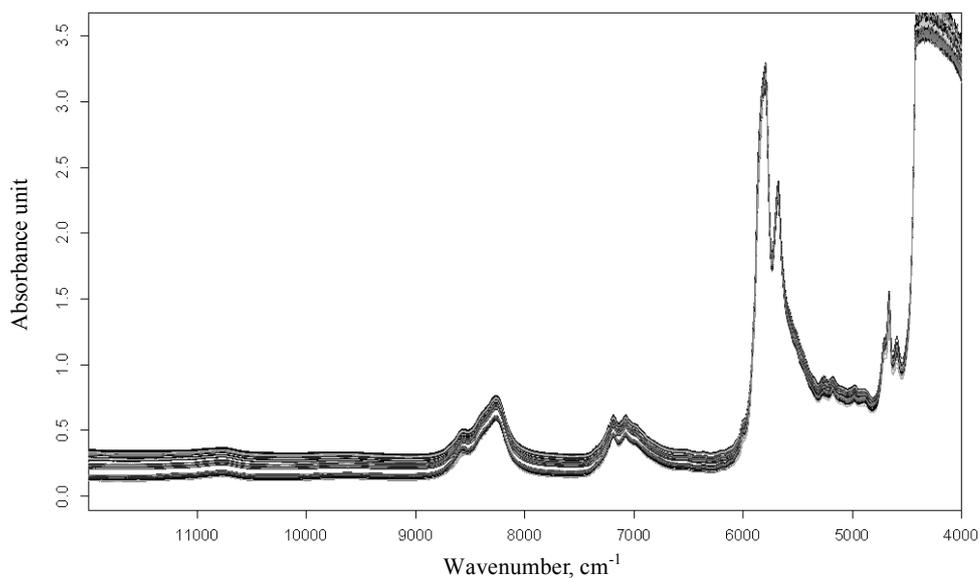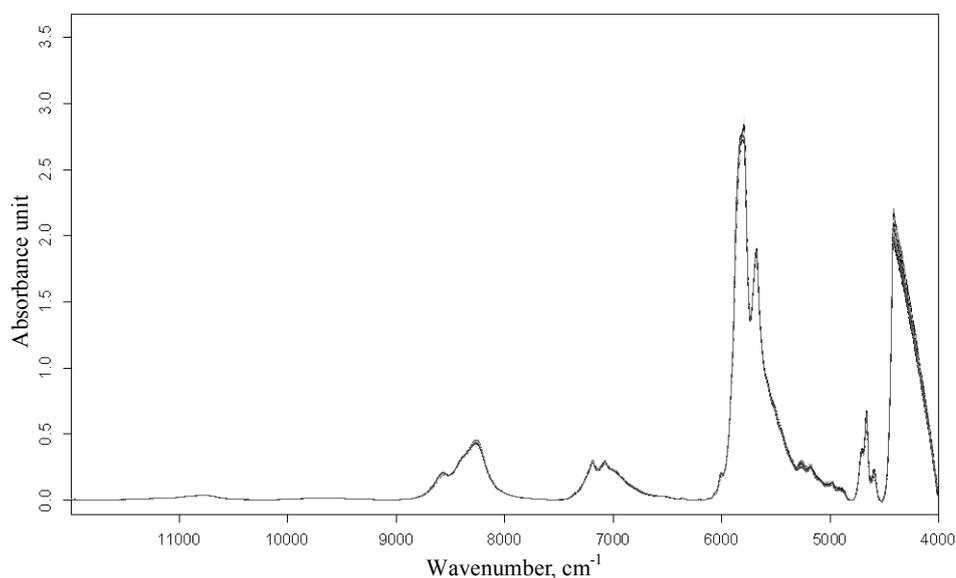

Figure 1: The raw spectrums of the samples

Figure 2: The manipulated spectrums of the samples

Calibration

In our experiment 36 rapeseed and 47 sunflower oil samples were used for calibration. For the better accuracy all samples were measured two times. To create the chemometric models OPUS software used the partial least-square (PLS) regression in cross validation mode. The advantage of this technique is that a stable, robust and accurate chemometric model could be created even if the calibration set contains fewer number of calibration samples. The goodness of a model could be expressed by the root mean square error of cross validation (RMSECV) and with the determination coefficient (R^2).

The better the model is the RMSECV more converges to zero and the R^2 more converges to 100%.

The chemometric models can be improved by model optimization. In the optimization process the software applies variations of many different mathematical data treatment method in different wavelength range (that we can set) to select the best approximation. The selection is based on the value of the RMSECV.

Results

Calibration results

After model optimization, the results of the best approximations are shown in *Figs 3-9*. These figures are the diagrammatic representation of the calibration results, where the true values of the vegetable oil properties were plotted as a function of the predicted values. The true values are the values that were determined by the appropriate EN ISO standard methods, the predicted values are estimated by NIR. In the figures the straight line represents the true, the dots represent the predicted values of the given property.
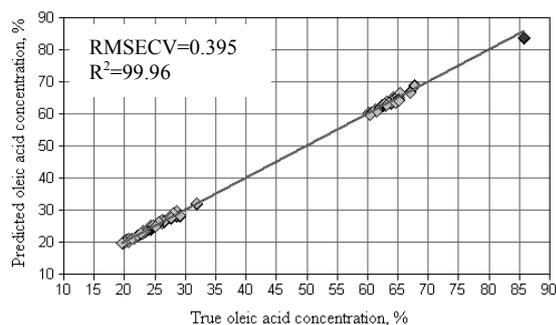

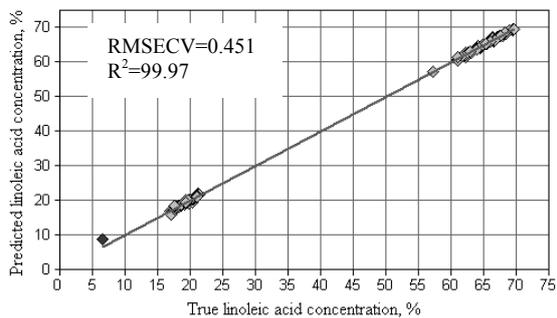*Figure 3:* The true concentration vs. predicted concentration values of oleic acid

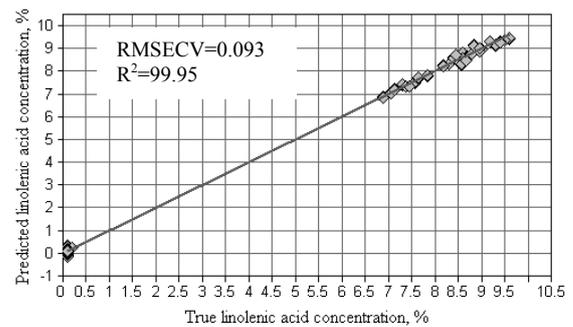*Figure 4:* The true concentration vs. predicted concentration values of linoleic acid

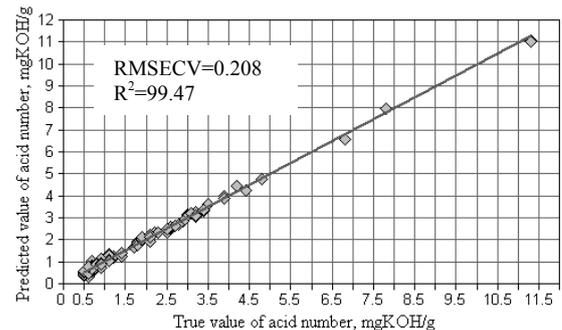*Figure 5:* The true concentration vs. predicted concentration values of linolenic acid

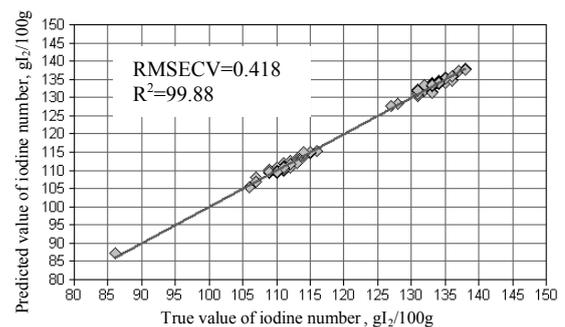*Figure 6:* The true vs. predicted values of acid number

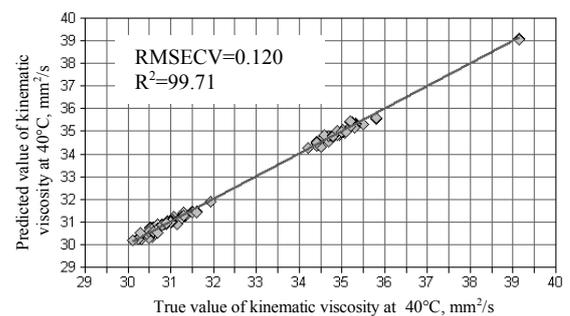*Figure 7:* The true vs. predicted values of iodine number

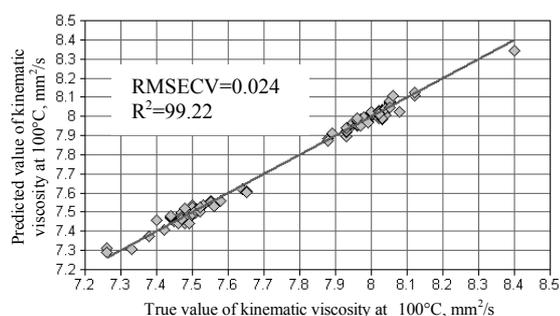*Figure 8:* The true vs. predicted values of kinematic viscosity at 40 °C

Figure 9: The true vs. predicted values of kinematic viscosity at 100 °C

The figures indicate that the dots match the straight line well enough, so the predicted values are very close to the true values in respect of all properties.

The numerical forms of the results are summarized in *Table 1*. In this table the RMSECV and R^2 values are shown for each property.

Table 1: The results of the calibration

Property	RMSECV	R^2, %
Oleic acid concentration	0.395	99.96
Linoleic acid concentration	0.451	99.97
Linolenic acid concentration	0.093	99.95
Acid number	0.208	99.47
Iodine value	0.418	99.88
Kinematic viscosity (40 °C)	0.120	99.71
Kinematic viscosity (100 °C)	0.024	99.22

Table 1 shows that the R^2 values are above 99% and the RMSECV values are under one in all cases.

According to the calibration results we found that the created calibration models are suitable for the determination of vegetable oil properties.

External validation results

In the course of external validation the established calibration models were tested with samples that properties are quantitatively known, and were excluded from the calibration set. As a result of this experiment the efficiency of the models could be concluded by the root mean squared error of prediction (RMSEP) and the determination coefficient (R^2). The better the prediction is the RMSEP more converges to zero and the R^2 more converges to 100%.

The external validation was executed with 51 different types of rapeseed and sunflower oil samples which spectrums were acquired with the same conditions that were applied at the calibration. The results of the experiment are shown in *Table 2*.

Table 2: The results of the external validation

Property	RMSEP	R^2, %
Oleic acid concentration	1.092	99. 89
Linoleic acid concentration	1.194	99.86
Linolenic acid concentration	0.234	99.88
Acid number	0.639	91.47
Iodine value	1.494	99.57
Kinematic viscosity (40 °C)	0.239	99.59
Kinematic viscosity (100 °C)	0.028	99.40

Apart from the acid number the R^2 values are higher than 99% in all cases and the RMSEP values are adequately small as well.

Conclusions

According to the results it may be concluded that the NIR technique is applicable for the determination of vegetable oil properties. The advantages of this method are the short analysis time, the non-destructive nature, no complex sample pre-treatment is needed and physical properties can also be determined. The difficulty of the technique is that calibration models must be created for the determinations with the help of a carefully collected calibration set.

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