

Feasibility of low cost non-destructive prediction of free fatty acids value of sunflower oil using near infrared spectroscopy

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Introduction

Along the food chain from farm to consumer, food commodities may be exposed to a multitude of hazards. As a result, they may undergo significant quality changes between the points of production and consumption. Confusion about the authentication of terms is widespread, and a complete agreement on the definition for characterisation of food products is not available in the literature. Authentication could be defined as “the assessment that a product strictly conforms to the legislation that is in force, in the countries where the product is marketed or sold”.¹ Studies on authentication of fats and oils through the distribution of fatty acids that are based on saturated, mono-saturated and poly-saturated fatty acids (SFA, MUFA and PUFA, respectively) can be done either by conventional chemical analysis² such as gas chromatography (GC), or by using the non-destructive and rapid technology of near infrared spectroscopy (NIRS) and chemometrics. In this paper we will show the results of free fatty acid (FFA) determination in sunflower oil, using a cost effective DAS spectrometer.

Materials and methods

Preparation of Samples

A set of 30 samples, drawn from the refinery outlet points at different segments of processing, were collected directly from the producers for analysis. The samples were partitioned into two groups, one group for spectral recording and the other for chemical analysis. Also 50 reference samples with various levels of FFA, from 0.01 to 4.0 %, were obtained from the Central Food

Technological Research Institute. As well, spectra were recorded for a further fifteen FFA reference samples and eight commercial samples, having less than 0.25 % FFA.

NIR spectral acquisition

An NIR Spectrometer with spectral range of 1050 to 1750 nm, and spectral resolution (FWHM) of less than 16 nm was used for acquisition of spectral data. Constant volumes of samples were exposed to the DAS instrument at predetermined height. The spectra were updated every 0.3 sec with average of 10 scans per reading. A total of 110 samples of sun flower oil from the refinery, commercial samples, and laboratory prepared samples, with FFA values from 0.025 to a maximum of 4.0 % were used for acquisition of the spectra in transmission mode.

Chemical analysis

Fatty acids are measured as their methyl esters, produced by esterification, neutralisation, and subsequent methylation, using a solution of HCL in methanol. The titrimetric² procedure of the AOCS.O.M No.Ca 5a-40 was used as standard method for FFA measurement.

Data analysis

NIR Spectroscopy coupled with appropriate chemometric techniques offers a fast, non-destructive and cost effective method for food analysis, and has the potential to be used on a wide range of products. It is being employed in the food industry to ensure that food products offered for sale meet the highest standard of food safety and hygiene, and to protect against fraudulent claims on the part of food producer, processor, distributor or retailers. NIR spectroscopy and chemometric methods provide the opportunity to deliver quality improvements and cost savings in the food industry, provided the technology is applied appropriately.³ Pre-treatment of the spectra is the most suitable method to ensure a good evaluation of the data embodied in the spectra. Hourant *et al.*⁴ demonstrated that absorbance at few wavelengths were sufficient for NIRS analysis of several sources of oils and fats. These workers showed high values of the correlation coefficient between absorbance and Iodine value (IV), calculated as the total unsaturation as determined by GC ($C16:1 + C18:1 + 2 * C18:2 + 3 * C18:3$). The absorbance wavelength regions were 1164 nm, 1664, 1714, and 1784 and 2116, 2144 and 2178 nm. Based on this for the present studies the wavelength region was segmented into two, as shown in Figure 1 after pre-processing for model building by what is referred to as the segmented method.

This reduces computing time during model building and yields good results, as reported in Table 1.

The spectral data were pre-processed by five methods, reported in Table 1. Finally the spectra were grouped into three sets, sixty for the training set, twenty each for the prediction, and validation sets. In the case of the training set, the spectral data were grouped through principal component analysis (PCA) with Hotelling T^2 as the boundary. The experiment also considered the effects of temperature. The samples were pre-heated using a Mettler balance (LP16) under pre-defined timing, and temperatures from 40°C to 65°C increasing in steps of five degrees. There was no noticeable difference between the patterns of the absorption spectra. It was reported by Azizian⁵ that a fixed temperature model responded reasonably well up to 35°C. Temperature fluctuation is taken care of in pre-processing by measuring the spectral data under wide range of temperatures.

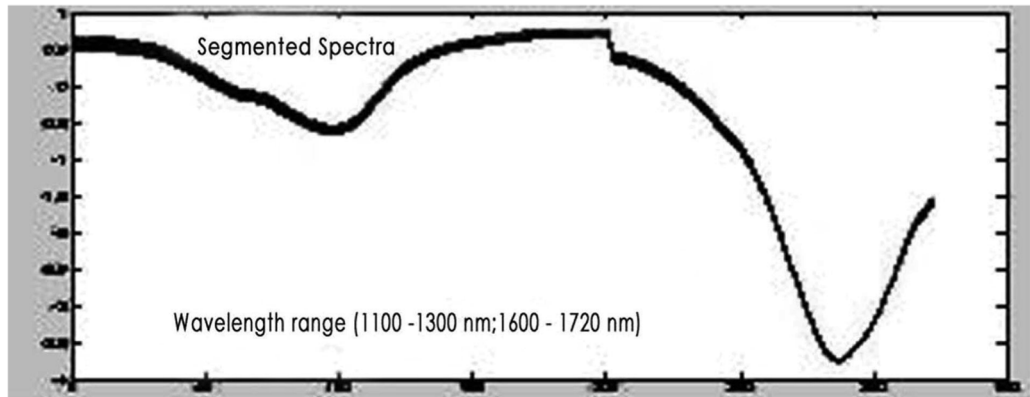


Figure 1. Segmented-preprocessed spectra.

This stabilises future NIRS measurements of oils or fats with regard to temperature effects. The training set was processed by partial least square (PLS) regression, with optimum latent variable selection. In this fourteen latent variables gave the most satisfactory calibration. Different pre-treatment combinations as reported in Table 1 were investigated. The results of these methods are tabulated. The prediction and validation sets, were used for verification of the calibration model by each method. PLS tool-box version 5.0 was used for model building. All programs were written under Matlab 6.5.

Results and discussion

Figures 2 and 3 show the spectral data, and calibration model results, while Table 1 shows the root mean square error of calibration (*RMSEC*), root mean square error of prediction (*RMSEP*) and root mean square error of validation (*RMSEV*) for sunflower oil. It was observed that using the derivative and segmented method of pre-treatment of the spectra the prediction of FFA had the

Table 1. Calibration results for free fatty acid value of sunflower oils.

No.	Pretreatment	<i>RMSEC</i>	Correlation	<i>RMSEP</i>	<i>RMSEV</i>
1	Baseline, smoothing, SNV	0.1297	0.9939	0.4170	0.6631
2	Baseline, smoothing, mean centre	0.1314	0.9938	0.4178	0.6783
3	Baseline, smoothing, derivative	0.0853	0.9974	0.2229	0.6931
4	Baseline, smoothing, range max.	0.1227	0.9946	0.4057	0.6944
5	Baseline, smoothing, SNV, segment	0.1616	0.9905	0.3209	0.6984

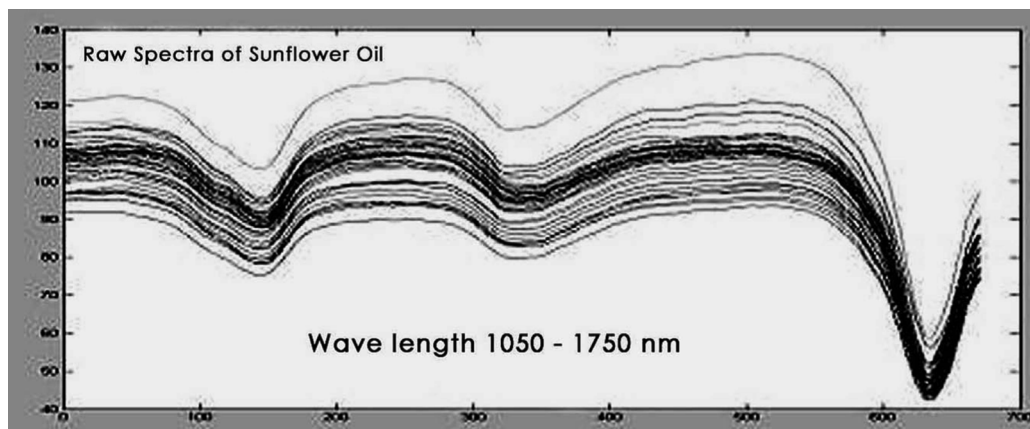


Figure 2. Raw spectra of Sunflower oil captured for different FFA values.

lowest *RMSEP* and *RMSEV* values. The same method could be implemented for prediction of FFA by on-line measurement. However, to predict the lowest ranges of FFA with higher sensitivity, a DAS spectrometer with a wider range (perhaps be 512 wavelength points) is suggested. It is suggested that range-based calibration would yield good results. The entire range could be applicable to both low and high level measurement of FFA. For such a range in FFAs the DAS with low cost, and with limited (128) wavelength points would have a very good correlation in high ranges of FFA of sunflower oil, but at the lower ranges the calibration would be less effective.

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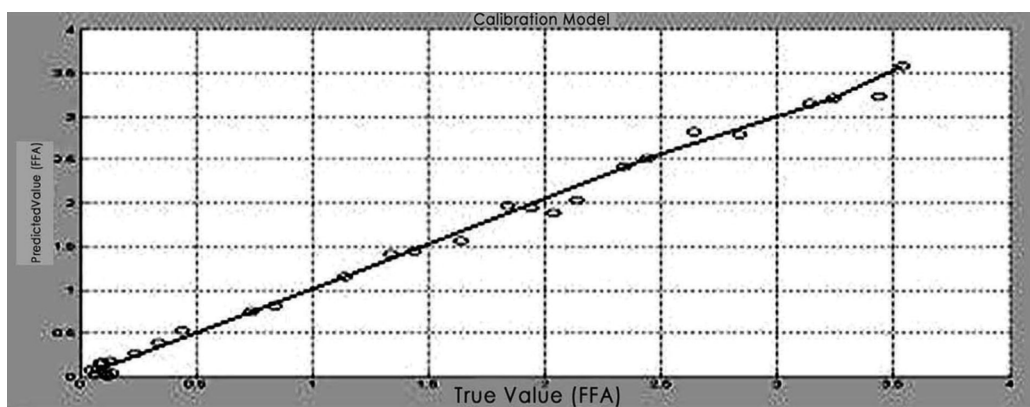


Figure 3. Calibration model output (True Value VS predicted value).

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