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Investigation of Frying Oil Quality Using VIS/NIR Hyperspectral Analysis

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Abstract Traditional chemical methods of analyzing frying oil quality are time-consuming and not amenable to on-line measurement. The main objective of this study was to evaluate quality changes of heated oils based on visible/near infrared spectral analysis using a hyperspectroradiometer. The reflectance spectra of the heated oils were analyzed within the range 400–1,750 nm. Acid value, total polar component, and viscosity of oil samples were used as indicators of different quality levels of oil. Partial least squares calibration models were developed for quantitative evaluations of these parameters. The R^2 and root mean square error for each prediction were calculated to assess the prediction capability of calibration models. The study demonstrated that using the established calibration models, quality parameters could be predicted with R^2 values over 0.92.

Keywords Spectroscopy · Fatty acid · Viscosity · Total polar component · Partial least squares method · Multivariate statistical analysis

Introduction

The fried food industry has been of great importance for the last two decades. Deep fat fried food products are popular due to their unique flavor and texture characteristics. During frying, oil is subjected to prolonged periods of heating at high temperatures of about 180 °C in the presence of air and water. This leads to a wide range of complex chemical reactions categorized as thermal oxidation, hydrolysis, and polymerization. Undesirable constituents and off-flavors are developed in frying oil due to these chemical reactions [1]. Therefore, the quality of the frying oil is a critical factor to maintain the high quality of fried products.

The rate of oil degradation during frying is influenced by several factors including the temperature of frying, exposure to air, stability of the oil against oxidation, and the moisture content of the fried food [2]. The frying industry is constantly seeking new frying oils that are stable and give desired characteristics to fried products. Thermal stability of the frying oil is related to the level of hydrogenation. The oxidative stability of the frying oil will increase with an increasing degree of hydrogenation. Thus, hydrogenated oils are widely used in the industry. However, during the hydrogenation process *trans* fatty acids are generated which, are associated with an increased risk of hazards to human health. This fact has become a major concern for the use of hydrogenated oil in the fried food industry. Recently, as an alternative to hydrogenated frying oil, partially hydrogenated oils with a lower degree of unsaturation are being increasingly adopted.

Degradation of oil during frying is followed by changes in free fatty acid (FFA) level, color, and viscosity, and by an increase in the number of polar molecules as a result of thermal and oxidative breakdown of the hydrocarbon chain in the oil [3]. It is vital that the quality of the frying oil is monitored closely in order to maintain a suitable quality for cooking oil-fried food. Some food service restaurants evaluate the oil quality from subjective parameters such as visual and odor characteristics [4].

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Traditional thermal methods for evaluating degraded oil quality (physical and chemical), such as measurement of total polar compounds (TPC), FFA, carbonyl value, and viscosity, are tedious, time consuming, and not amenable to on-line assessment. A highly increasing consumption of edible oils in deep-fat frying industry demands rapid, accurate, and cost-effective techniques for oil quality control.

Many studies have been conducted to investigate the potentials of spectroscopic methods to determine quality parameters in edible oils, these include determination of *trans* fat content and the peroxide value of edible oil using Fourier transform near-infrared spectroscopy (FT-NIR) [5, 6].

Innawong et al. (2004) [7] used the spectra within the range of 4,000–850 cm^{-1} with a FTIR attenuated total reflectance spectroscopy (FTIR–ATR) to differentiate among good, marginal, and unacceptable oils.

Near-infrared spectroscopy instruments are also recognized as effective tools for quality control in the food industry due to their fast and non-destructive measurements, there are no requirement for using hazardous reagents and solvents, and there can be more flexible sample handling.

The goal of this study was to investigate the feasibility of the VIS/NIRS techniques for rapid, quantitative evaluations of quality parameters for hydrogenated and non-hydrogenated oil that have gone through heating cycles. The specific objectives of this study were:

1. To establish VIS/NIRS calibration models to predict acid value, viscosity, and total polar components of heated oils,
2. To select the best wavelength regions for predicting the three quality parameters, and
3. To test and validate the prediction accuracy of the developed calibration models.

Experimental Procedures

Oil Sample Preparation

Hydrogenated and non-hydrogenated soybean oils were obtained from a local supplier (Pars Oil Manufacturing Factory, Iran). The hydrogenated and non-hydrogenated oils were blended in the ratios (w/w %) of 0:100 (i.e. non-hydrogenated oil), 40:60 and 80:20 to form three mixtures of oil samples. All the oil samples were heated to 190 °C in a domestic fryer on a 9 h per day cycle for a total time of 72 h. The temperature of the oil was controlled automatically by a controller (Model 689000-01, Eutech Instrument Pte Ltd., Singapore). Samples of 200 ml were collected at the end of each daily heating cycle and were kept at 4 °C before being used for chemical analysis and spectral collection.

Chemical Tests

Three major quality parameters of each oil sample, FFA value, viscosity, and TPC, were measured and used as indicators of oil quality. The TPC of the samples was determined according to the AOCS official method, Cd 20-91, by column chromatography (AOCS [8]). The efficiency of fractionation was assessed by thin layer chromatography and results were recorded in percentages of polar compounds (m/m).

The acid value of samples was measured according to the AOCS official method, Cd 3a-63, by alkaline titration. The acid value was recorde in milligrams of KOH per gram of sample (AOCS [8]). The viscosity of the samples was measured using a controlled stress/shear rheometer with coaxial concentric cylinder with a built-in peltier plate (Advanced rheometer, AR 2000, TA Instruments Inc., Leatherhead, UK) at 40 °C. Viscosity readings were reported in Pa s.

Spectral Data Acquisition

Spectral data were acquired using a portable hyperspectroradiometer (FieldSpec®, Oilseeds Cultural Development Research Institute, Tehran, Iran), which measured reflectance spectra over a wavelength range of 350–2,500 nm and a spectral resolution of 3 nm.

During spectral measurement, a Petri dish filled with an oil sample (40 ml) was placed underneath the fiber bundle of the FieldSpec® Pro at a distance of 20 cm. The distance was calculated based on the field of view of 18 of the fiber bundle. A DC regulated fiber-optic illuminator (Fiber-Lite PL900-A, Dolan–Jenner Industries Inc., MA, USA) was used as the light source. Two fiber-optic light-guiding branches were mounted on a test frame to guide light to the sample. Figure 1 shows the test platform for spectral data collections.

Light reflected from the sample was collected by the fiber-optic bundle and sent to the Field Spec® Pro for intensity measurement. A white reference panel with approximately 100% reflectance across the entire spectrum was used as a reference standard. At each wavelength reading, a ratio between the light intensity from the sample and the white reference was calculated. The View Spec Pro software (Analytical Spectral Devices, Boulder, CO, USA) was used for instrument control and computation. All spectra were recorded and stored on a PC. The spectral range of each spectrum was 350–2,500 nm. The reflectance was normalized so that the values were within the range of 0–1.
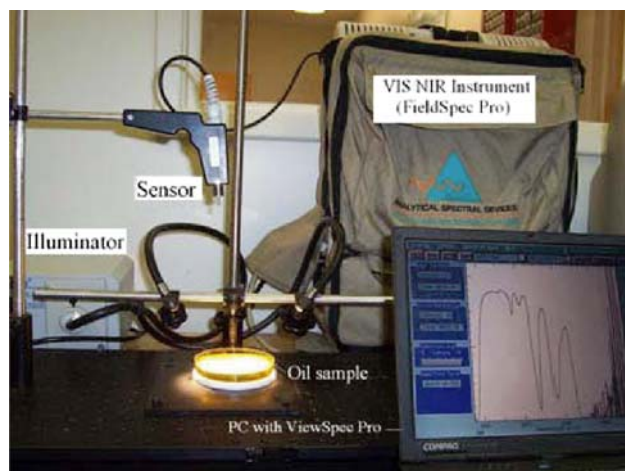
Fig. 1 Experimental setup for spectral data collection

Calibration and Data Analysis

Spectral analysis was conducted using GRAMS/AI v7.02 (Thermo Electron Corp., Salem, NH, USA). Due to significant noise bands observed in the ranges of 350–400 and 750–2,500 nm, for all the spectra, only the spectral range of 400–1,750 nm were used for calibration and data analysis. Out of a total number of 54 spectra, 36 were randomly selected to training set and were used to develop partial least squares (PLS) calibration models. The remaining 18 spectra formed a validation set to verify the prediction capability of the calibration models.

The PLS calibration method was used to decompose the spectra into a set of so-called variation spectra, also called factors, that represent changes in reflectance within the spectral range. It performed the decomposition on both spectral and targeted parameter(s) simultaneously, so that the calibration models established are related directly to the parameters of interest. In this study, three parameters, acid value, viscosity, and TPC of the oil samples, measured with the chemical analysis, were used as "constituent" data, and the spectra were used as the "spectral" data for the training set. These spectra were preprocessed using mean centering and automatic baseline correction (Thermo Galactic [9]).

Mean centering is a process of calculating the average spectrum of the training set spectra and then subtracting the average spectrum from each individual spectrum. The same procedure was performed on the concentration values of each constituent. This enhanced the difference between samples in both spectral and constituent data by removing the mean from the data. Automatic baseline correction was chosen to remove the baseline effects from the spectra occurringt during spectral collection. The PLS procedure yielded the calibration models, the optimal numbers of factors used in the calibration models, the feature wavelengths for predicting the constituents, and the predicted

constituents for each sample in the training set. The optimal number of factors for establishing the calibration model was determined by the predicted residual error sum of squares (PRESS). The number of factors with the minimum PRESS value was considered the optimal. Beta coefficients were used to find the feature wavelength ranges (at peak or valley in the PLS beta coefficients plot) to predict the parameter of the interest in an oil sample.

Eliminating the useless wavelength regions which had no or very little contribution to parameter prediction would simplify the calibration models and reduce the time for required computation. Also selected wavelength regions can be used as a basis to design on-line systems with lower costs.

Concentration residuals, the difference between the actual and predicted concentration for samples, were used for outlier detection in a training set. The best calibration model was chosen with the highest R^2 values for the predicted parameters versus actual parameters obtained from cross validation. The root mean square error (RMSE) for both training and validation sets was calculated for each constituent to evaluate prediction performance of the calibration model.

Results and Discussion

Chemical Analysis

Figures 2, 3 and 4 show changes in acid value, viscosity and TPC, respectively, during heating three types of oil samples, namely non-hydrogenated (0:100), 40%
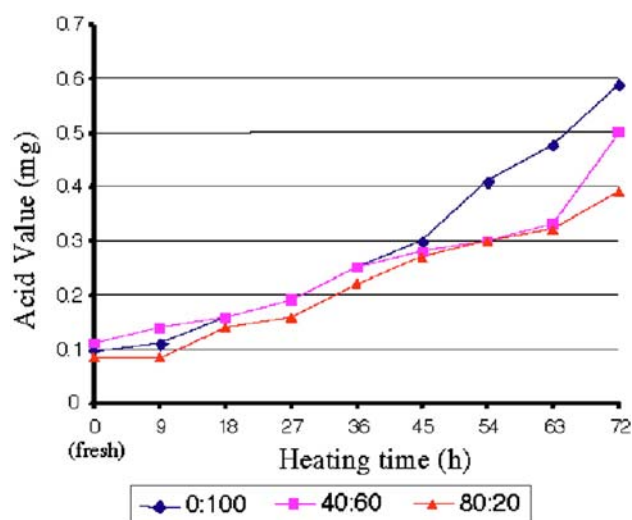

Fig. 2 Changes in acid values during heating for three types of oil samples, namely non-hydrogenated (0:100), 40% hydrogenated (40:60) and 80% hydrogenated (80:20)
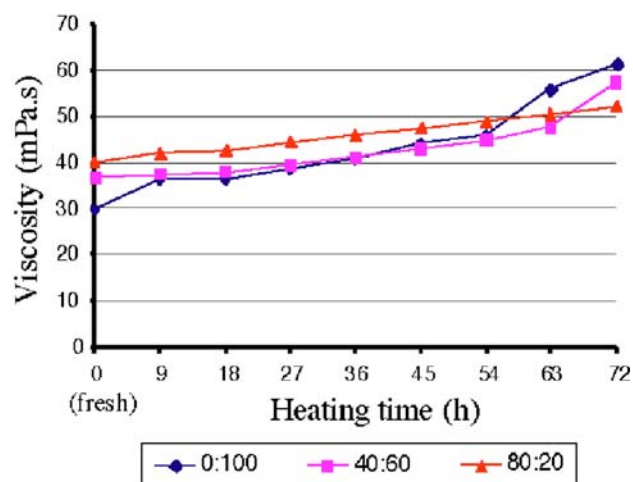
Fig. 3 Changes in viscosity during heating for three types of oil samples, namely non-hydrogenated (0:100), 40% hydrogenated (40:60) and 80% hydrogenated (80:20)
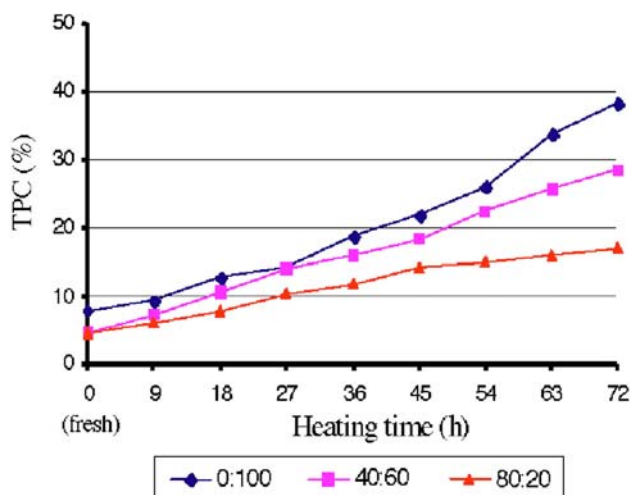

Fig. 4 Changes in total polar compounds during heating for three types of oil samples, namely non-hydrogenated (0:100), 40% hydrogenated (40:60) and 80% hydrogenated (80:20)

hydrogenated (40:60) and 80% hydrogenated (80:20). For a fresh oil sample, the average initial acid value was 0.1 mg KOH/g fat, whereas the average viscosity and TPC values were 36 mPa s and 6%, respectively. The viscosity, TPC and acid values were in the typical range reported for fresh good quality vegetable oils [10–12].

Values of the quality parameters increased with heating time, indicating increased oxidation and polymerization. The quality of the non-hydrogenated oil changed more rapidly, as expected, compared to the oils with higher degrees of hydrogenation. This is attributed to the higher content of unsaturated fatty acids in the non-hydrogenated oil resulting higher oxidation during heating. Based on regulations in

most countries, frying oil that has gone through heating cycles should be discarded when its TPC value reaches 25% (Benedito et al. [10]). Results of chemical analysis demonstrated that the 0:100 and 40:60 oils reached the 25% TPC level within the 72 h of frying at 190 °C used in this study. This would have occurred within an even shorter time if the oil was used for frying foods. Therefore, in this study, different levels of oil quality from the fresh to the discardable stage, were generated. This would justify the applicability of the results of this study for quality determination of oils that have been used for frying foods.

VIS/NIR Calibration

Figure 5, as an example, shows a reflectance spectrum of non-hydrogenated (0:100) soybean oil within the range of 400–1,750 nm. The differences among the reflectance spectra of the three types of oil samples were not significant visually, except for those in the visible range (400–700 nm) due to color changes of the oil samples during heating.

Model 1: Calibration Model Using a Spectral Range of 400–1,750 nm

PLS calibration models were established to predict acid value, viscosity, and TPC with the number of factors at 9, 8, and 8, respectively. Results of the calibration are shown in Figs. 6, 7 and 8. The acid value was predicted to be 0.95 for the training set and RMSE of 0.0042 and 0.0111 for the training R^2 and validation sets, respectively. The viscosity was predicted with a R^2 of 0.91 for the training set and RMSE of 0.0005 and 0.0007 for the training and validation sets, respectively. The TPC was predicted with a R^2 of 0.98 for the training set and RMSE of 0.3080 and 0.7505 for the training and validation sets, respectively.
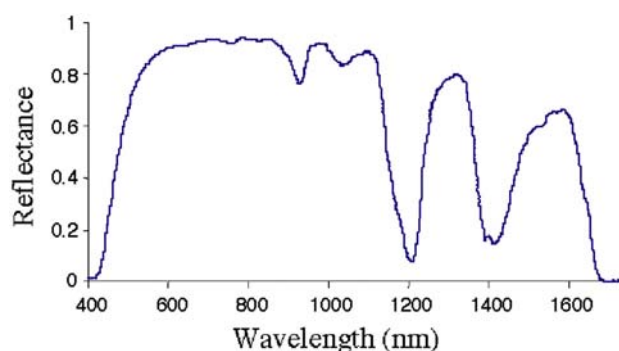

Fig. 5 A reflectance spectrum of non-hydrogenated (0:100) soybean oil within the range of 400–1,750 nm
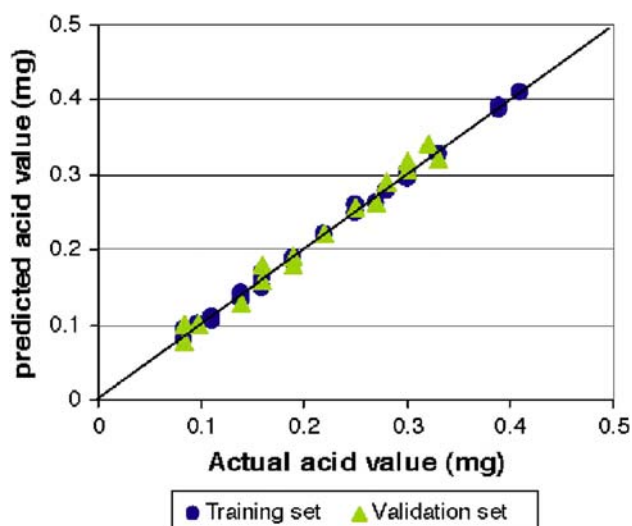
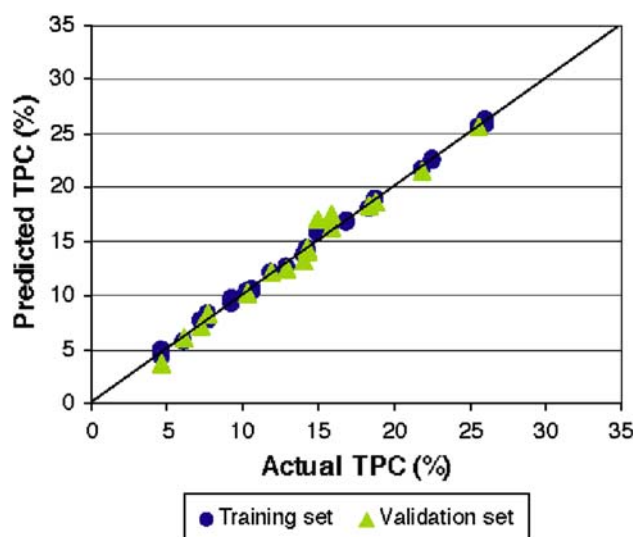Fig. 6 Predicted versus actual acid value of the training and validation sets

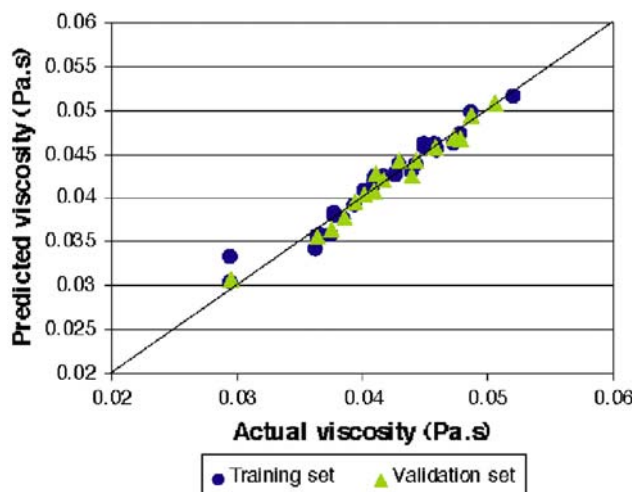Fig. 8 Predicted versus actual total polar compounds for the training and validation sets

Fig. 7 Predicted versus actual viscosity for the training and validation sets

Model 2: Calibration Models Using the Feature Wavelength Ranges

Based on the PLS beta coefficient plot for each constituent, the common spectral regions of the most variations (named, feature wavelength ranges) were found within the ranges of 450–550, 850–950, 1,140–1,180 and 1,200–1,300 nm. Variations in the visible region could be due to the color changes in oils heated for different times. Lankmayr et al. [13] studied the region of 410–445 nm to classify two categories of pumpkin seed oil according to their quality, namely accepted and rejected oil. Acceptable oils had higher peaks at 418 nm and lower peaks at 434 nm compared to rejected oils.

The second overtone of C–H stretching in various chemical groups such as CH_2, CH_3 and HC=CH is observed in the region of 1,100–1,300 nm [1]. The bands around 1,180 nm have been assigned to the C–H stretching overtone in HC=CH structure of pure fatty acids containing *cis* double bonds [14]. The region of 9,100–7,560 cm^{-1} (about 1,098–1,322 nm) was reported to contain information about the degree of unsaturation and was used for quantitative determination of Iodine value of edible oils [15]. Li et al. (2000) [10] related the region of 8,975–7,189 cm^{-1} (around 1,114–1,391 nm) to the *trans* content of edible oils.

The bands of C=O also appeared at around 900 nm. The observed variations on the PLS beta coefficient plot within the feature wavelength ranges could be explained by the fact that the C=C bonds break down during thermal degradation of the oil and *cis* double bonds transform to *trans* double bonds. Oxidation products with a C=O group in their structure also were formed as a result of thermal oxidation.

The second calibration model was established using the reflectance within the feature wavelength ranges [16]. With the similar procedures of previous calibrations, the cross-validation results for predicting acid value, viscosity, and TPC for three types of oil samples are shown in Figs. 9, 10, and 11, respectively. With the training set, the acid value, viscosity, and TPC predicted with an R^2 of 0.93, 0.92 and 0.92, and RMSE of 0.0190, 0.0011, and 1.4030, respectively. The RMSE of the validation sets for the acid value, viscosity, and TPC were 0.0183, 0.0008, and 1.3101, respectively.
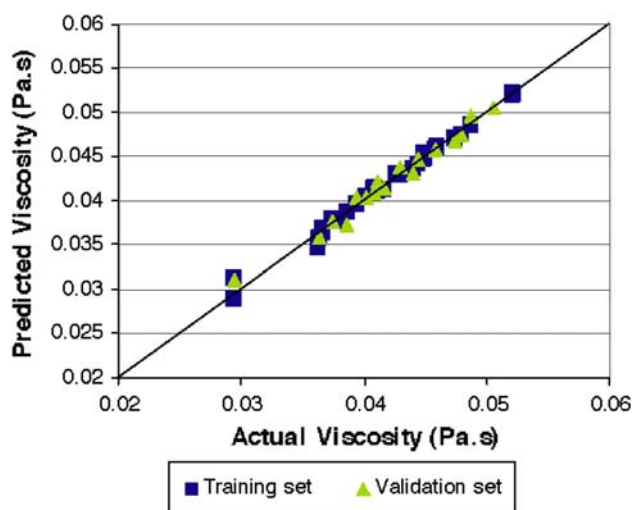
Fig. 9 Predicted versus actual acid value using the PLS calibration models with the feature wavelength ranges
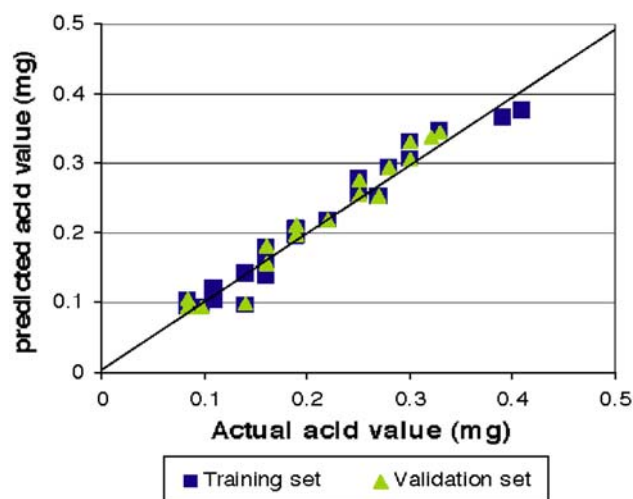

Fig. 10 Predicted versus actual viscosity using the PLS calibration models with the feature wavelength ranges

Table 1 summarizes the calibration models developed and corresponding cross-validation results for predicting the three quality parameters.
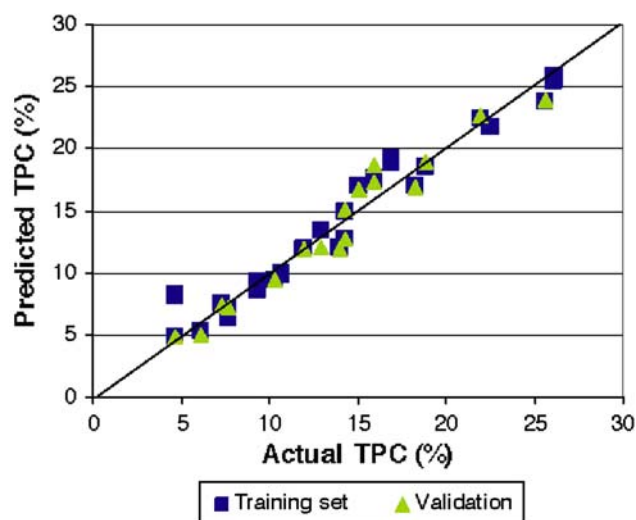

Fig. 11 Predicted versus actual total polar compounds using the PLS calibration models with the feature wavelength ranges

Conclusions

The feasibility of using VIS/NIRS techniques to rapidly and quantitatively evaluate quality parameters for heated edible oils was investigated. The results show that with a fine resolution, the spectral reflectance of the oils can be used to effectively predict the three quality parameters, i.e. acid value, TPC, and viscosity.

Partial least squares calibration models using a wavelength range of 400–1,750 nm were able to track the changes of the three parameters of the heated oil samples with high accuracy R^2 values obtained from the calibration models were 0.95 for acid value, 0.91 for viscosity and 0.98 for TPC.

Four feature wavelength ranges, 450–550, 850–950, 1,140–1,180 and 1,200–1,300 nm, were selected. The R^2 values for predicting the three quality parameters were above 0.92. The feature wavelength ranges could be used as a basis for designing on-line oil quality evaluation systems.

In summary, the VIS/NIR spectroscopy has proven itself to be a useful and fast technique with the capability of simultaneous prediction of oil quality parameters. Once a

Table 1 Summarized results of PLS calibration models

Calibration model	Training set						Validation set		
	R^2			RMSE			RMSE		
	AV	VI	TPC	AV	VI	TPC	AV	VI	TPC
Model 1	0.95	0.91	0.98	0.0042	0.0005	0.30	0.0111	0.0007	0.7505
Model 2	0.93	0.92	0.92	0.0190	0.0011	1.40	0.0183	0.0008	1.3101

AV acid value, *VI* viscosity, *TPC* total polar component

calibration model has been developed, prediction and analysis could be done within a few minutes.

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