

Near-Infrared Spectroscopic Determination of Degradation in Vegetable Oils Used To Fry Various Foods

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ABSTRACT: Near-infrared (NIR) spectroscopic methods for measuring degradation products, including total polar materials (TPMs) and free fatty acids (FFAs), in soy-based frying oil used for frying various foods have been successfully developed. Calibration models were developed using forward stepwise multiple linear regression (FSMLR) and partial least-squares (PLS) regression techniques and then tested with an independent set of validation samples. The results show that the quality of oil used for frying different foods can be measured with a single model. First-derivative treatments improved results for TPM measurement. In addition, PLS models gave better prediction results than FSMLR models. For PLS models, the best correlations (r) between the NIR-predicted data and the chemical method data for TPMs and FFAs in oils were 0.995 and 0.981, respectively. For FSMLR models, the best r values for TPMs and FFAs in oils were 0.993 and 0.963, respectively.

KEYWORDS: NIR, free fatty acids, total polar materials, forward stepwise multiple linear regression (FSMLR), partial least-squares (PLS) regression, frying oil quality

INTRODUCTION

Deep-fat frying is a popular method of food preparation. One reason is that deep-fat-fried foods have unique flavor and texture combinations. In addition, deep-fat frying is easy and fast. Foods are cooked rapidly in oil at high temperature, and the quality of fried foods is closely connected to the quality of the frying oil.¹ Upon heating in the presence of moisture and oxygen, frying oil is subject to a series of degradation reactions, such as hydrolysis, oxidation, and polymerization.^{2,3} The compounds generated from these reactions not only have negative effects on the flavor of fried products but also have antinutritional properties and form potential carcinogenic compounds.^{3–5} Thus, frying oil quality control is important.

Chemical analyses are reliable ways to measure the degradation of frying oil. However, these chemical methods are often time-consuming and costly, require potentially hazardous reagents, and generate chemical waste. In addition, these chemical methods are usually not capable of online quality assessment. To overcome these drawbacks, spectroscopic methods have been investigated as alternatives to chemical methods.^{6–15}

Among all chemical parameters, total polar materials (TPMs) and free fatty acids (FFAs) are most widely used as reliable chemical indicators of frying oil degradation.^{2,16–19} In a previous study in our laboratory,¹² TPM and FFA contents in soy-based frying oils heated with added water were successfully measured by near-infrared (NIR) transmission spectroscopy. Recent papers by other researchers have also shown that NIR spectroscopy can successfully measure TPM and FFA in soy oils used to prepare French-fried potatoes.¹⁴

The study described here builds on our earlier research¹² that demonstrated the ability of NIR spectroscopy to successfully monitor the thermal degradation of soy oil. However, that study involved only oil heated in the presence of pure water and did not evaluate oils actually used to fry foods. Some foods may introduce new lipids into the system and interfere with the spectroscopic

determination. The study described here was conducted to determine whether frying different types of foods in a soy-based frying oil affects the reliability of TPM and FFA measurements made by NIR spectroscopy. In addition, the potential of using a single calibration model to measure the quality of oil used to fry various foods was evaluated in this study.

MATERIALS AND METHODS

Sample Preparation. FryMax 3500, a commercial soy-based frying oil distributed by ACH Food Co. Inc. (Memphis, TN), was obtained from a local Sam's Club store or from a local food wholesale distributor (Cash-Wa Distributing). To include possible processing variations in oils, two different lots of FryMax frying oils were purchased at different times. Oil samples with different levels of degradation were generated by heating the oils for 8 h per day at approximately 190 °C in Presto fryers (model 0600308) while frying 50 g per hour of fresh maize tortilla chips (made in the UNL pilot plant), partially precooked potato fries (HyVee Brand), or partially precooked breaded chicken nuggets (Banquet Brand). Only a single food product was fried in a given batch of oil, with aliquots removed at 4 h intervals during heating. A total of six heating runs were made, using the two lots of oil and three food products.

Aliquots removed for spectroscopic and TPM analyses were stored in brown glass bottles under nitrogen to prevent further oxidation and kept in a freezer at –8 °C until analyzed. Chemical analyses for FFA measurement were performed on the day that the oil was collected.

Chemical Methods. The chemical methods used in a previous study¹² for measuring TPMs and FFAs were used in the present study. All chemical analyses were carried out in duplicate. Free fatty acid contents were determined by titration with standard 0.01 N NaOH and phenolphthalein using AOCS Official Method Ca 5a-40.²⁰

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Table 1. Characteristics of Reference Data for Calibration and Validation Sets

sample set	no. of samples	constituent range (%)	
		TPMs	FFAs
calibration	120	1.53–40.97	0.015–0.491
validation	66	2.10–31.35	0.025–0.393

Total polar materials were determined by solid phase extraction. TPM was defined as the amount of material remaining on a 500 mg silica column after elution of a 0.5 g sample with 50 mL of a 90:10 mixture of petroleum and diethyl ethers. First, a 500 mg silica SPE cartridge (Alltech, part 22935) was conditioned with 10 mL of the elution solvent. Then 0.5 g of oil was dissolved in 5 mL of elution solvent. The sample solution was transferred to the cartridge and eluted with 50 mL of elution solvent, and the eluent was collected in a tared 125 mL round-bottom flask using a vacuum manifold. The solvent was evaporated from the flask with a vacuum evaporator at 8 °C, and the final traces of solvent were removed in a vacuum oven at 60 °C for 60 min. Finally, the flask containing the nonpolar fraction eluted from the cartridge was weighed. The content of polar compounds, in percent, was calculated using the formula

$$\text{total polar materials, \%} = [(m - m_1)/m] \times 100$$

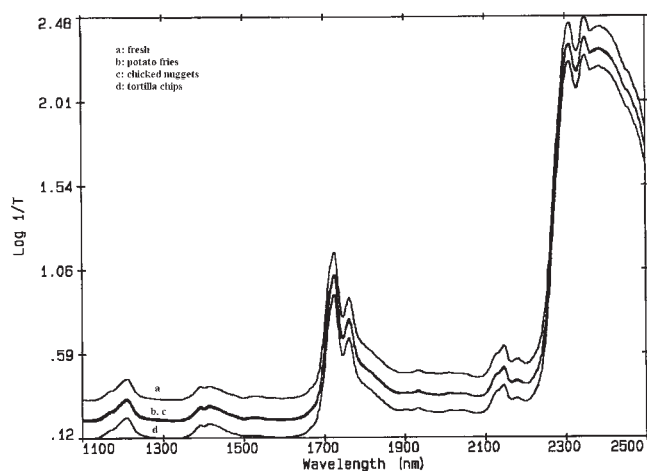
where m_1 = mass of the nonpolar fraction (g) and m = mass of sample (g).

NIR Spectroscopy. The spectra of oils used to fry various foods were collected with a Foss NIRSystems model 6500 scanning spectrometer using NSAS software for instrument control and calibration development (NIRSystems Division of Foss Electric, Silver Spring, MD), as previously described.¹² Spectra were collected in $\log(1/T)$ format from each oil as direct transmission measurements over a 400–2500 nm range, where T is the transmittance of a sample at a specific wavelength.

Due to temperature effects on spectral response,²¹ all spectra were collected under the same conditions. Because this frying oil is semisolid at temperatures up to 54 °C, individual aliquots were heated to 60 °C in a water bath to completely liquefy the oil prior to collection of spectral data. Then each aliquot was placed into a 2 mm path length quartz cuvette,²¹ and the cuvette was inserted into the holder in the instrument. The spectrum of each aliquot was obtained by immediately collecting and averaging 32 individual spectral scans.

Calibration Development and Validation. Thirty-one aliquots, including fresh oil, were collected from each batch of heating with a specific food, such that a total of 62 oil samples per food were generated from the two lots of oil. These samples were then divided into 40 member and 22 member sets by random selection. After that, the 40 member sets from each food were combined to form a 120 member calibration set, and the 22 member sets from each food were combined to form a 66 member validation set. In addition, the calibration sample set was inspected to ensure that the extremes of TPM and FFA values were included.

Multivariate statistical methods were used to create calibration models correlating the NIR data and chemical parameters. Calibration models were created using forward stepwise multiple linear regression (FSMLR) and partial least-squares (PLS) regression. Because of the possibility of improving results by separating overlapping bands, first- and second-derivative treatments were also applied to the spectra prior to calibration development, with parameters of wavelength gap and segment length optimized. On the basis of results from the previous study¹² and unpublished work from our laboratory on models using the shorter wavelength (<1100 nm) region, all calibration models were developed using a range of 1100–2500 nm. The correlation coefficient of calibration (R), standard error of calibration (SEC), and mean square error of cross-validation (MSECV) for PLS were used to determine the

**Figure 1.** NIR spectra of fresh oil and degraded oils from each food.

optimal number of wavelengths (FSMLR) or terms (PLS) to be included in a calibration model. To prevent overfitting of the FSMLR models, a maximum of four wavelengths was used. In general, more terms may be used in PLS models than wavelengths in FSMLR models without overfitting, because there is no correlation among the PLS factors.

Each model generated from the $\log(1/T)$ data, or the first and second derivatives of $\log(1/T)$, was validated with the 66 member sample set not used for calibration development. The correlation coefficient of prediction (r) and root-mean-square of the differences (rmsd) were used to choose the best models. Because the TPM and FFA values had different ranges, the relative predictive determinant (RPD) value was useful in comparing the results of TPM and FFA predictions. The RPD is a simple statistic that enables the evaluation of a standard error of prediction (SEP) or rmsd in terms of the standard deviation (SD) of the reference data of the prediction set.²²

RESULTS

Chemical Determination of Frying Oil Degradation Products. Before heating, the FFA and TPM values of the two lots of FryMax frying oils, as determined by the reference methods, ranged from 0.015 to 0.024% and from 1.53 to 2.11%, respectively.

Characteristics of the reference data for calibration and validation sets are listed in Table 1. TPMs have been widely used to measure deterioration of frying oils and are considered to include all non-triacylglycerol or altered triacylglycerol materials in the oil, as well as polar materials released from foods, according to AOCS Cd 20-91.²⁰ The TPM values increased linearly with increased heating time, and the rate of increase was not affected by the type of food.

FFAs are the main degradation products of hydrolysis. FFA content is a measure of the amount of fatty acid chains hydrolyzed off the glycerol backbone.¹⁹ Generally, FFA values increased with an increase in frying time, but fluctuations were observed due to the easy degradation of FFAs by heat, oxidation, and light into other polar compounds.^{23,24}

NIR Spectra. Figure 1 shows the NIR spectra of fresh and highly degraded soybean-based frying oil samples that were used to fry fresh tortilla chips, partially precooked potato fries, or partially precooked breaded chicken nuggets. Bands >2300 nm appear distorted due to the extremely strong absorptions in this region. Differences in the spectra are observable in Figure 1. Some differences in the shapes of the spectra of fresh and

Table 2. FSMLR and PLS Analysis Results for TPMs

data treatment	wavelength (nm) or no. of factors	calibration		validation			
		multiple R	SEC (%)	<i>r</i>	rmsd (%)	slope	RPD
FSMLR							
log(1/ <i>T</i>)	1420, 1712, 1766, 2254	0.998	0.67	0.992	0.91	1.026	7.85
first derivative (segment 40 nm, gap 40 nm)	1366, 1822, 2004, 2190	0.997	0.83	0.993	0.88	1.010	8.12
second derivative (segment 30 nm, gap 20 nm)	1390, 1746, 1982, 2136	0.997	0.82	0.992	0.91	1.022	7.83
PLS ^a							
log(1/ <i>T</i>)	9	0.998	0.64	0.994	0.78	1.001	9.39
first derivative (segment 40 nm, gap 40 nm)	8	0.998	0.66	0.995	0.72	1.001	9.81
second derivative (segment 30 nm, gap 20 nm)	7	0.998	0.72	0.993	0.82	0.996	8.70

^a 1100–2250 nm.

Table 3. FSMLR and PLS Analysis Results for FFAs

data treatment	wavelength (nm) or no. of factors	calibration		validation			
		multiple R	SEC (%)	<i>r</i>	rmsd (%)	slope	RPD
FSMLR							
log(1/ <i>T</i>)	1100, 1320, 1712, 2186	0.979	0.027	0.963	0.025	1.015	3.64
first derivative (segment 40 nm, gap 40 nm)	1132, 1902, 2446	0.967	0.033	0.955	0.027	0.949	3.32
second derivative (segment 30 nm, gap 20 nm)	1478, 1766, 2026, 2166	0.975	0.029	0.949	0.029	1.011	3.15
PLS ^a							
log(1/ <i>T</i>)	10	0.991	0.018	0.981	0.018	0.981	5.15
first derivative (segment 40 nm, gap 40 nm)	8	0.988	0.021	0.977	0.019	0.996	4.72
second derivative (segment 30 nm, gap 20 nm)	10	0.989	0.020	0.977	0.020	0.991	4.65

^a 1100–2250 nm.

degraded oils are observable. The appearance of a more prominent shoulder between 1800 and 1900 nm can be noted in the spectra of the degraded oils. Also, small differences in the spectra can be seen between 2000 and 2150 nm. Previously, Büning-Pfaue and Kehraus⁸ reported that observable differences between spectra of fresh and degraded oils over a 2040–2118 nm range were due to the presence of degradation products in oxidized oils.

Osborne et al.²⁵ indicated that the major NIR absorption bands in a fat or oil are centered at 1200 nm for a CH₂ second overtone, at 1734 and 1765 nm for CH₂ first overtones, and at 2310 and 2345 nm for CH₂ stretch–bend combinations. Besides these major absorption bands, absorptions around 1700 nm are due to first overtones of C–H stretching vibrations, and absorptions at 1400, 2072, and 2078 nm are due to first overtones of O–H stretches and combinations of O–H stretching and deformation. Osborne et al.²⁵ also indicated that absorption bands at 2140 and 2190 nm are due to cis-unsaturated fatty acid units and can be used to estimate the degree of unsaturation of a fat/oil.

NIR and TPMs. The NIR predicted data were highly correlated with the reference method data for TPMs in both the calibration and validation sets (Table 2). Although PLS models using the longer wavelength region did not predict TPMs better than FSMLR models in the previous study,¹² PLS models gave improved results for TPMs compared to FSMLR models in the present study. Compared to FSMLR models, higher *r* and lower rmsd values were obtained by PLS models, such that *r* values ranged from 0.993 to 0.995 and rmsd values from 0.72 to 0.82%. The results show that a PLS model using the first-derivative

of log(1/*T*) gave slightly improved results compared to the PLS models using the original log(1/*T*) or second-derivative of log(1/*T*). When using the first-derivative of log(1/*T*), the *r* value between the NIR predicted data and reference method data for the validation set was 0.995, and the rmsd value for the validation set was 0.72%. In the present study, excluding the wavelength region >2250 nm from the PLS models improved the results. This may be because the region above 2250 nm does not contain any useful information about the constituent of interest, but does add noise to the models.

When using FSMLR regression to develop calibration models, the first-derivative treatment also provided better results than the original log(1/*T*) or the second-derivative treatments. When using the first-derivative spectra, the *r* value between the NIR predicted data and reference method data for the validation set was 0.993, and the rmsd value for the validation set was 0.88%. Wavelengths of 1366, 1822, 2004, and 2190 nm were chosen by the program as the key wavelengths for measuring TPM values when using first-derivative spectra.

NIR and FFAs. There were strong correlations between the NIR predicted data and reference method data, but the correlations were not as strong as for the TPM values (Table 3). Similar to TPM results, the PLS models gave improved results compared to the FSMLR models, with *r* values ranging from 0.977 to 0.981 and rmsd values from 0.018 to 0.020%. A difference from TPM results was that the models using derivative spectra did not give better prediction than models using original log(1/*T*) spectra. When using log(1/*T*) spectra in a 10 term PLS calibration, an *R* value of 0.991 and a SEC value of 0.018% were obtained.

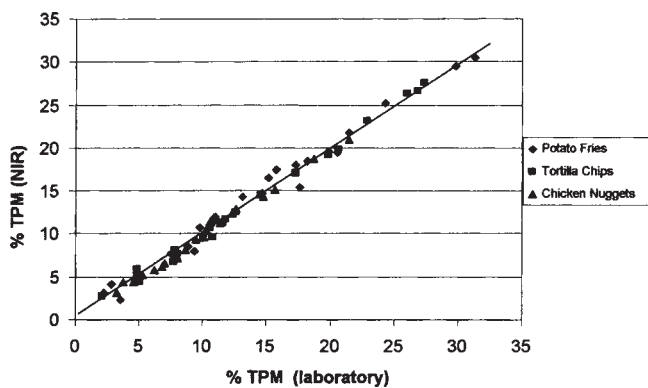


Figure 2. Scatter plot diagram comparing TPMs of validation set samples, as determined by PLS calibration using the first derivative of $\log(1/T)$, to TPMs as determined by the reference method.

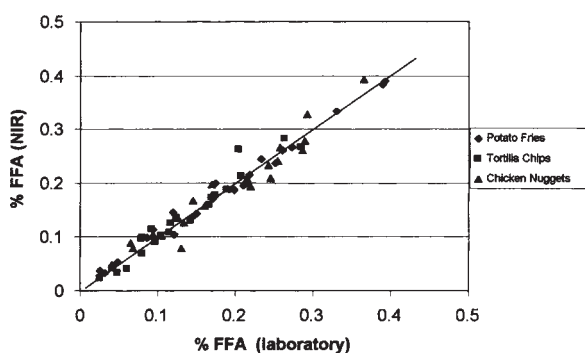


Figure 3. Scatter plot diagram comparing FFAs of validation set samples, as determined by PLS calibration using $\log(1/T)$, to FFAs as determined by the reference method.

When this model was used to predict FFA values, the r value between the NIR predicted data and reference data was 0.981 and the rmsd value was 0.018%.

First- and second-derivative treatments also did not give improved results when using FSMLR to estimate FFA contents in frying oils. When using the original $\log(1/T)$ spectra in an FSMLR calibration, the R value was 0.979 and the SEC was 0.027%. An r value of 0.963 and an rmsd value of 0.025% were obtained when using this model for FFA prediction. Wavelengths of 1100, 1320, 1712, and 2186 nm were chosen as the key wavelengths for measuring FFAs.

DISCUSSION

Validation results from the best models for TPM and FFA measurement are also shown as scatter plots comparing NIR predicted data and reference method data (Figures 2 and 3). The slopes of the X – Y scatter plots comparing NIR predicted data and reference method data were close to 1 (Tables 2 and 3), indicating that the models successfully measured the full range of TPMs and FFAs in the validation samples. In addition, data points from oils used to fry the three different foods, as shown in Figures 2 and 3, were located close to the 45° line, meaning that the models performed similarly with oils used to fry different foods. Overall, FFA predictions were not as good as the TPM predictions, as demonstrated by comparing their RPD values (Tables 2 and 3). Factors that may cause the weaker results for FFAs have been previously discussed¹² and include greater uncertainty in

the chemical data for FFAs,²³ and the fact that FFAs are relatively unstable and easily converted to other polar compound.²⁴ In addition, PLS models gave better results than FSMLR models in the present study. PLS models allow the use of all relevant wavelengths, rather than only the few wavelengths permitted in FSMLR models, and often provide improved results.²⁶

In summary, NIR calibration models have been successfully developed to directly measure TPM and FFA values in soy-based frying oil used to fry various foods. These results confirm and expand upon our previous findings, for which NIR spectroscopy was used to measure TPM and FFA values in oil heated only with water.¹² On the basis of the results of this study, the following conclusions can be made: (a) predictions of TPMs were better than the predictions of FFAs; (b) PLS models were better than FSMLR models for predicting both TPMs and FFAs; (c) a first-derivative treatment generally was most useful for TPM predictions, but was not beneficial for FFA measurement; (d) the quality of an oil used to fry various foods can be quantitatively measured with a single model; and (e) high values of r and low values of rmsd were obtained in this study, meaning that NIR is effective in measuring TPM and FFA values in soy-based frying oil.

Once an instrument is precalibrated, TPMs and FFAs in frying oils can be quantitatively measured by NIR in <3 min. The NIR method is fast, simple, accurate, and nondestructive. Additionally, it is environmentally friendly because no chemical wastes are produced. Finally, the NIR method is more adaptable to at-line or online quality assessment than conventional methods. Further study may generate a universal method for oils from multiple sources by including additional oils in the calibration model.

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