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ORIGINAL PAPER

Rapid Determination of Degradation in Frying Oils with Near-Infrared Spectroscopy

Jose A. Gerde · Connie L. Hardy · Charles R. Hurburgh Jr · Pamela J. White

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Abstract Measures of free fatty acids (FFA), total polar materials (TPM), and conjugated dienoic acids (CDA), typical indices of oil degradation, were analyzed in daily oil aliquots taken from soybean oils with different linolenic acid concentrations used to fry French fries. The oils also were scanned with a reflectance near-infrared spectrometer using a wavelength range of 350–2,500 nm. By using partial least squares and one-out cross validation, calibrations were developed to quantitatively determine FFA, TPM, and CDA by near-infrared spectroscopy (NIRS). The coefficients of determination (R^2) when compared to the standard methods were 0.973 for FFA, 0.984 for TPM, and 0.902 for CDA. NIRS was an accurate and fast method to determine FFA, TPM, and CDA in oxidized oils. The ability to obtain different parameters simultaneously makes NIRS a potentially valuable tool for food quality assurance.

Keywords Calibration · Conjugated dienoic fatty acids · Free fatty acids · Frying · NIR spectroscopy · Soybean oil · Total polar material

Introduction

The frying industry uses several parameters to predict the quality of oil in deep-fat fryers. Acidity expressed as free fatty acids (FFA) content is a common procedure [1] for measuring triglyceride hydrolysis during deep-fat frying. The method has been modified to use small oil samples to reduce cost and waste [2], but both the modified and official AOCS methods are titration procedures, with a colorimetric end point. The subjectivity of judging the end point means it is difficult to get consistency among different laboratories and operators, and even from an individual operator.

Total polar material (TPM) content [1] is also a reliable indicator of frying oil deterioration. TPM uses hazardous organic solvents (petroleum ether and diethyl ether) and requires 3.5 h per sample [3]; thus, the index is more often used in research studies rather than in regular quality control.

The level of conjugated dienoic fatty acids (CDA, [1]) in a polyunsaturated oil is an indicator of initial oxidation. This index is not commonly used by the food industry but is very useful in scientific studies. Measurement of CDA is done by spectrophotometry.

Near-infrared spectroscopy (NIRS), a clean, fast, and nondestructive technique, has been proven to be useful in determining fatty acid composition in soybeans [4]. It also

J. A. Gerde · P. J. White (✉)
Department of Food Science and Human Nutrition,
2312 Food Sciences Building, Iowa State University,
Ames, IA 50011-1060, USA
e-mail: pjwhite@iastate.edu

J. A. Gerde
e-mail: jgerde@iastate.edu

C. L. Hardy
Value Added Agriculture Program, Iowa State University,
Ames, IA 50011, USA
e-mail: chardy@iastate.edu

C. R. Hurburgh Jr
Agricultural and Biosystems Engineering,
1541 Food Sciences Building, Iowa State University,
Ames, IA 50011-1060, USA

C. R. Hurburgh Jr
Department of Agricultural and Biosystems Engineering,
Iowa State University, Ames, IA 50011, USA
e-mail: tatry@iastate.edu

has been used to determine the quality of edible oils [5–7]. Previous work by Ng et al. [8] showed strong correlations between FFA and transmission spectra NIRS of oils heated at 190 °C with water added (to promote the formation of FFA and TPM). The FFA range was 0.020–0.568% oleic acid. Relative predictive determinants (RPD), were 2.5 and 6.0 for FFA, and 15.3 and 19.7 for TPM calibrations for each of two validation sets. For TPM, the oil samples ranged between 2.2 and 62.9% polar material. It is generally accepted that a calibration with an RPD $\geq$ 5.0 is good and can be applied in quality control operations; if the RPD is $\geq$ 8.1 the calibration can be used in any application [9].

Büning-Pfaue and Kehraus [10] developed multiple partial least squares (PLS) models for FFA in the range of 0.03–2.76% as oleic acid and for TPM in the range of 7.6–48.1%. RPD were 5.5 for the FFA calibration and 5.0 for the TPM calibration. In this case, the oils being tested were obtained from actual fryers in restaurants and bars. They used reflectance spectroscopy to scan the samples with a Buhler/BUECHI Spectrometer in the transflection mode. Yildiz et al. [11] reported a PLS calibration for CDA determination in soybean oils using transmittance NIRS, with RPD of 3.6 and 4.5 for two path lengths.

The previous studies were limited because the oxidation of the oils was done by heating and pumping water into the oils or by inducing the oxidation with a fluorescent lamp [8, 11]. For the one study done with actual frying oils [10] the number of samples used was small (n = 33 for FFA and n = 20 for TPM). The objectives of the current study were to determine FFA, TPM, and CDA with NIRS in actual frying oils with usage ranges typical of the food service.

Materials and Methods

This NIRS study was conducted as part of a frying stability test of oils with varying levels of linolenic acid [12].

Oils

Extruded-expelled, physically refined soybean oils with three levels of linolenic acid were obtained through Innovative Growers from American Natural Soy, Inc., Cherokee, Iowa. The cultivars from which the low-linolenic acid oils came were: (1) IA2064 produced by Taylor Seeds, Inc. near Hartley, IA in 2003 (ultra low-linolenic acid oil, ULL) and (2) IA3018 produced by Pleasant Valley Farms near Iowa City, IA, in 2004 (low linolenic acid oil, LL). The third oil was obtained from conventional beans produced by American Natural Soy (Control, Ctrl). The starting linolenic acid contents of the oils were: 1.5 (ULL), 2.6 (LL), and 5.3% (Ctrl) as previously measured [12]. The two lines with reduced content of linolenic acid originated from Iowa State University soybean varieties developed through traditional breeding practices.

French Fries

Extra-long (XL) fancy 0.635-cm (1/4 inches) shoestring par-fried frozen French fries were obtained from a commercial supplier. The fries were par-fried by the processor in partially hydrogenated shortening (canola and/or soybean oil) and/or palm oil, and/or beef fat. They also contained dihydrogen phosphate (to retain color), dextrose, and natural flavoring.

Frying Operation

Three Star Twin-Pot deep-fat fryers model 530TA (Star Manufacturing International Inc., St Louis, MO, USA, 7.2 l per well) were used. Oil treatments were run in duplicate and French fries were fried for 23 days according to Gerde et al. [12]. The oil in the fryers was filtered and replenished to the starting level with the appropriate fresh oil type after each day of frying.

Oil Sampling

Aliquots from the filtered oils were taken at the end of each frying day for further analysis. The samples were stored at –22 °C in glass jars under nitrogen in the dark to prevent further oxidation.

Free Fatty Acids

The FFA content was measured daily from the oil aliquots (n = 141) by titration using a modification of the AOCS Official Method Ca 5a-40 [1] for small samples [2]. The acidity was expressed as percentage of oleic acid.

Total Polar Compounds

Total polar compound (TPC) content was measured by column chromatography with AOCS Method Cd 20–91[1]. The TPC content was measured on the fresh oils and after days 1, 2, 5, 6, 9, 11, 14, 16, 19, 21, and 23, (n = 69).

Conjugated Dienoic Fatty Acids

The CDA content was determined as described in the AOCS Official Method Ti 1a-64 [1]. The sample was dissolved in isooctane and the absorbance of the solution was measured in a UV-Vis spectrophotometer (U-2000 Double-Beam UV/Vis Spectrophotometer, Hitachi Instruments, Inc., Tokyo, Japan) at 233 nm. The concentration of oil needs to be adjusted to fit the absorbance values between 0.2 and 0.8 [3]. CDA were measured in the fresh oils and in the oils after 2, 5, 6, 9, 11, 14, 16, 19, 21, and 23 days of frying (*n* = 63).

Near-Infrared Spectroscopy

Daily oil aliquots were allowed to come to room temperature in the dark and poured into 64/51 mm approximate internal diameter top/base weighing dishes (Fisherbrand, Fisher Scientific, Pittsburgh, PA, catalogue number 02-202B). They were scanned with a reflectance spectrometer using a wavelength range of 350–2500 nm (LabSpec Pro, Analytical Spectral Devices, Boulder, CO, USA). The samples were tested after cooling; the test did not include temperature compensation.

Spectra were analyzed with Unscrambler 9.6 using PLS modeling. The optimal FFA and TPM models used three Principal Components (PC) and the optimal CDA model used nine PC. Wavelengths in the range of 445–1,675 nm were selected for CDA and TPM analyses and 1,141–1,675 nm for FFA analysis. These ranges contained the most useful information about the parameters measured. The validity of the models was evaluated by cross validation.

Results and Discussion

Free Fatty Acids

The FFA levels of the measured oil aliquots were 0.07–4.65% oleic acid equivalent, with an average of 1.76%. The best PLS model (3 PC) using one-out cross validation yielded a coefficient of determination (R^2) of 0.973 and a standard error of cross validation (SECV) of 0.232 with an RPD of 6.2. Five out of the 141 aliquots were removed as spectral outliers, but no particular oil type or frying stage showed a tendency to produce spectral outliers. Figure 1 shows the regression between the reference and the predicted values.

Total Polar Compounds

The number of aliquots used for the TPM calibration was 69, rather than the 141 used for the FFA calibration, because of the time and resources needed to analyze all the samples. The TPM contents of the samples used ranged between 2.6 and 35.4%, with a mean of 25.5%. The highest TPM value was far above the 24–27% maximum allowable level accepted by many countries for frying oils [13]. Figure 2 shows the regression curve between the reference and the predicted values. The best PLS model yielded an R^2 of 0.984 with a SECV of 1.068 and an RPD of 8.0. Seven outliers were removed, with no tendency for a particular stage to produce more outliers.

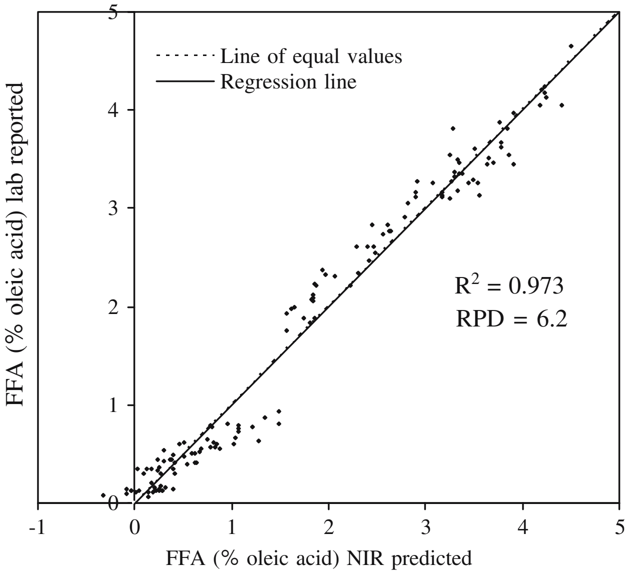

Fig. 1 Relationship between the lab-reported and the NIRS-determined free fatty acid values (cross validation). R^2 coefficient of determination, *RPD* relative predictive determinant

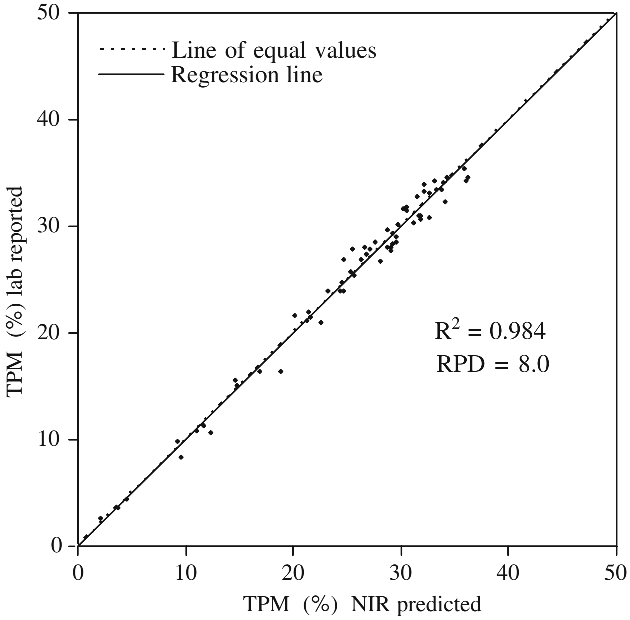

Fig. 2 Relationship between the lab-reported and the NIRS-determined total polar material values (cross validation). R^2 coefficient of determination, *RPD* relative predictive determinant

Conjugated Dienoic Fatty Acids

Figure 3 shows the regression curve between the reference CDA method and the predicted values. The R^2 for

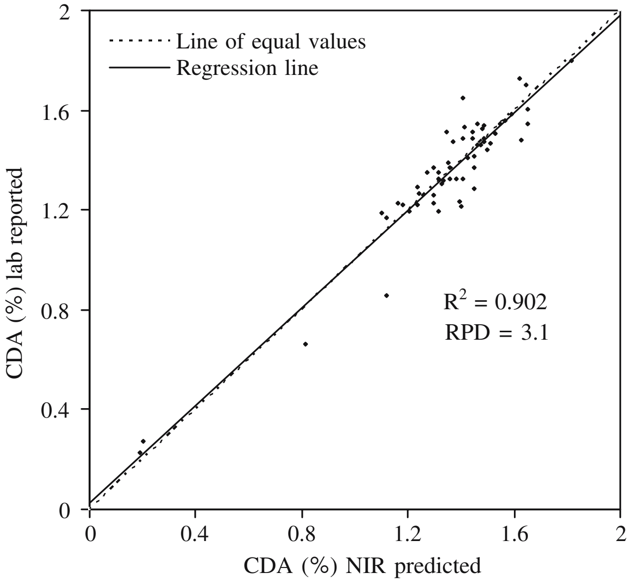

Fig. 3 Relationship between the lab-reported and the NIRS-determined conjugated dienoic acid values (cross validation). R^2 coefficient of determination, *RPD* relative predictive determinant

this model was 0.902 with a SECV of 0.088 and an RPD of 3.1. The range of CDA measured in the oil was from 0.23 to 1.80%, with a mean of 1.35%. Four outliers were removed.

In general, the tested samples had a wider range of FFA and CDA than was used in previous work [9, 11], however the range of TPM was narrower. Reflectance NIRS is a reliable, accurate and fast technique to determine the FFA, TPM, and CDA concentrations in actual frying oils during lengthy use. Because there is no need for extensive sample preparation or use of solvents or chemicals, NIR spectroscopy might be adapted for real-time quality control purposes at frying operations in the food industry.

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