A New Spectrophotometric Method for the Rapid Assessment of Deep Frying Oil Quality

Xin-Qing Xu*

Food Science Australia, Werribee, Victoria 3030, Australia

ABSTRACT: A new and quick spectrophotometric method was developed to assess deep-frying oil quality. The scanned spectrophotometric curves of the frying oil samples from 350 and 650 nm wavelength changed systematically with the duration of deep frying. The absorbances of the frying oil samples, especially those measured at 490 nm, increased significantly during frying and were significantly correlated to frying time ($r \geq 0.95$, $P < 0.001$). There was a strong correlation between the absorbances of a set of oil samples taken from 0 to 80 h of deep frying and total polar compound contents in the same set of oil samples analyzed using the American Oil Chemists' Society official method ($r = 0.974$, $P < 0.001$). The equation for conversion of the absorbances to total polar compound contents is $y = -2.7865x^2 + 23.782x + 1.0309$. The absorbances of 10 different types of frying oils with samples taken from 0 to 80 h of deep frying in duplicate were also strongly correlated to total polar compounds in the same oil samples ($r = 0.953$, $P < 0.001$, $n = 220$). The results show that this method is fast, simple, convenient, and reliable.

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KEY WORDS: Deep frying, frying oil, oil quality, quick test, spectrophotometry, total polar compounds.

Frying oil, used continuously or repeatedly at high temperatures, is subject to a series of degradation reactions and formation of a variety of decomposition compounds. These decomposition compounds have negative effects on the quality of the frying oil and the flavor and nutritional value of the fried food. Some of these compounds may also be harmful to human health (1). There are regulations in some countries for discarding overused oils (2). Therefore, oil quality control during deep frying is essential for the food industry. A variety of methods are available for assessing degradation of frying oil. Chemical analyses measure decomposition compounds reliably in the frying oil (3), but are time-consuming, costly, and usually require reasonable analytical expertise. To date, there are a few quick tests available in the commercial market for measuring oil degradation that provide reliable results (4). Spectroscopic methods are fast and convenient and have the potential to replace chemical analyses (5). This paper presents a newly developed spectrophotometric method for the rapid assessment of oil quality during deep frying.

*Address correspondence at Food Science Australia, Private Bag 16, Werribee, VIC 3030, Australia. E-mail: xinqing.xu@foodscience.afisc.csiro.au

EXPERIMENTAL PROCEDURES

This quick method of assessing frying oil quality used oil samples from two evaluation studies (6,7) of new lines of canola oils in deep-frying applications at Food Science Australia. Detailed information related to chemical and physical analyses, sensory evaluation, and research results was described in References 6 and 7.

Oil samples and potato chips. In the first study (6), six oils were used to fry potato chips (French fries) over two replicates of 80-h trials. The oils were three high-oleic canola oils containing 2.5, 4.4, and 6.8% linolenic acid, respectively, and a sunflower oil (supplied by Ag-Seed Research Pty. Ltd., Horsham, Australia); a palm olein and a partially hydrogenated canola oil (supplied by EOI Foods, Sydney, Australia). In the second study (7), four oils were used over two replicates of 80-h trials: a high-oleic canola oil (supplied by Ag-Seed Research), a commercial palm olein (supplied by Meadow Lea Foods, Melbourne, Australia) and two blends of palm olein and canola oil (PC 70:30 and CP 30:70, vol/vol). Each trial lasted 10 d (8 h frying/d).

Quick-frozen potato chips (straight cut, 13 mm in height and width and 10 cm in length on average; Edgell, Grade A, Melbourne, Australia) were used in the two studies. ("Quick-frozen potato chips" is the terminology used in Australia. The appropriate terminology should be French fries.) These had been precooked by the manufacturer in refined tallow for 1 min and were stored at −18°C before use. Oils (7.5 L/each) were placed in Roband fryers with a temperature control (manufactured by Woodson Australia Pty. Ltd., Melbourne, Australia) and not topped-up over 80 h of deep frying. The oil was heated to 190 ± 2°C and kept at this temperature for 8 h/d. To minimize other effects on oil quality, the oils were not filtered, and only those floating objects on the top of the oils were removed daily. Potato chips (200 g) were fried in each oil for 3.5 min and six times per hour from 11:00 A.M. to 1:00 P.M. on days 1, 4, 6, 8 and 10 for each trial, and 100 g of chips were fried for 5 min and three times per hour in the other frying time. Oil samples (~100 mL) for analysis were taken at the end of the day and stored at −32°C.

Total polar compounds. The contents of total polar compounds (TPC) in a set of 11 oil samples taken from day 0 to day 10 of the high-oleic canola containing 6.8% linolenic acid were analyzed using the American Oil Chemists' Society (AOCS) Official Method Cd 20-91: Determination of Polar

Compounds in Frying Fats (8). TPM VERI-FRY® PRO quick test (Test Kit Technologies, Libra Technologies Inc., Metuchen, NJ) was used to measure TPC in all the oil samples. The TPC values measured by the AOCS official method were used to calibrate the quick test results (4).

To investigate the relationship of polar compound contents in oils and spectrophotometric absorbances of the oils, known amounts of polar compounds collected from the analysis of total polar compounds using the AOCS Official Method Cd 20-91 (8) were mixed with unused canola oil and then measured at 490 nm. The unused oil served as a control.

Spectrophotometric measurement. Oil samples were placed in a standard disposable cuvette (1 cm optical path) and warmed in a 60°C oven for 15 min before measuring the spectrophotometric absorbance using a Hitachi U-2000 Spectrophotometer (Tokyo, Japan). The spectrophotometer absorbance was zeroed against air without using any cuvette. The oil samples were scanned from 350 to 650 nm wavelength. Both the scanned curves of each frying oil sample and the absorbance values of each oil sample recorded at 10 nm intervals were obtained.

Statistical analysis of data. The data were statistically analyzed using *t*-test, *F*-test, correlation and regression. The curves and the equations of the curves in the following figures were fitted using Microsoft Excel, Version 97 (Redmond, WA).

RESULTS AND DISCUSSION

In the two separate studies, 10 different types of oils were heated for 80 h at 190°C with potato chips (French fries). The scanned spectrophotometric curves of four oils, as representatives of the 10 oils, are shown in Figures 1 to 4. All the oils and their replicates had a similar pattern as shown in the figures, but with different values for the individual oils. It is evident from the scanned curves that each frying oil showed systematic changes in spectrophotometric absorbance. These changes are most evident between the wavelengths of 470 and 500 nm. Using a high-oleic canola oil containing 2.5% linolenic acid (LA) as an example, the absorbance changes of the oils over 80 h of frying are shown in Figure 5. The absorbances measured at 470, 480, 490, and 500 nm, respectively, all increased significantly during frying and were all significantly correlated with frying time ($r \geq 0.95$, $P < 0.001$). Among these wavelengths, the absorbances measured at 490 nm had the highest r^2 value (≥0.992) for most of the oils tested, and consequently this wavelength was chosen for this method.

To verify if this quick test can distinguish the quality difference of the same type of oil with different fatty acid profiles, we tested three high-oleic canola oils with major differences in the levels of linoleic acid and LA (6). The spectrophotometric absorbances of the oils measured at 490 nm are shown in Figure 6. The absorbances of the three oils were similar initially, all increased significantly during frying, and were strongly correlated with frying time ($r \geq 0.99$, $P < 0.001$). The canola oil containing 2.5% LA had significantly better oxidative stability (measured by TPC and acid value) and better sensory ranking

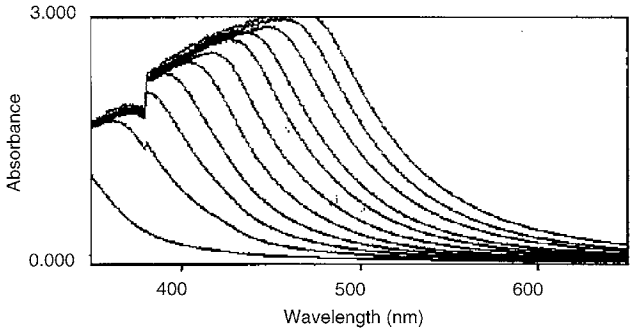

FIG. 1. Effect of frying time on absorbance of the canola oil containing 2.5% linolenic acid. The scanned wavelengths were from 350 to 650 nm. The lowest absorbance curve at the bottom of this figure represents the unused oil. The curves from the second-lowest absorbance to the highest absorbance represent oil samples taken from 1 to 10 d of deep frying (8 h/d), respectively.

for the potato chips (French fries) fried in the oil than the oils containing 4.4 and 6.8% LA, respectively. In addition, the canola oil containing 4.4% LA also had significantly better oxidative stability and better sensory ranking for the chips fried in the oil than the oil containing 6.8% LA (6). Analysis of the data using *t*-test for paired samples for means showed that the absorbances in the three oils with samples taken from 0 to 80 h of frying were significantly different from each other ($P < 0.001$). The canola oil containing 2.5% LA had the lowest rate of increase and the oil containing 6.8% LA had the highest rate of increase among the three oils. This indicates that the spectrophotometric absorbance of frying oil measured at 490 nm is a good parameter to use to characterize oil quality.

Chemical analysis is the most reliable way to measure decomposition compounds in frying oil. Among these methods, measurement of TPC in frying oil is the most popular (3). A set of canola oil samples taken from 0 to 80 h of deep frying were analyzed using the AOCS official method for determination of TPC (8). The results were used to calibrate this spectrophotometric method. There was a strong correlation ($r = 0.974$, $P < 0.001$) between the absorbance and TPC contents in the same

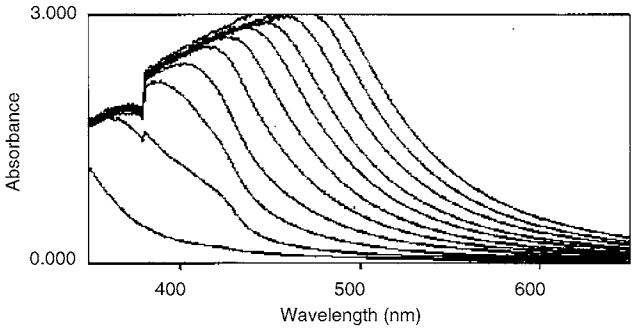

FIG. 2. Effect of frying time (day) on absorbance of the canola oil containing 6.8% linolenic acid. The scanned wavelengths were from 350 to 650 nm. The lowest absorbance curve at the bottom of this figure represents the unused oil. The curves from the second-lowest absorbance to the highest absorbance represent the oil samples taken from 1 to 10 d of deep frying (8 h/d), respectively.

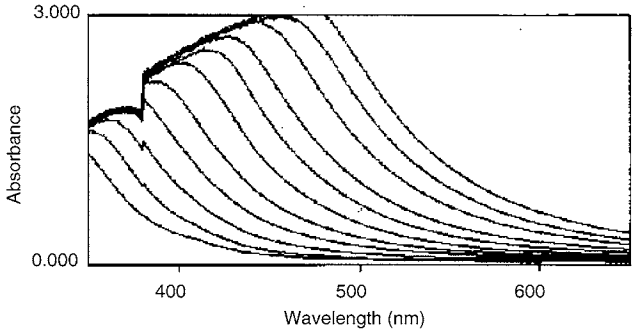

FIG. 3. Effect of frying time on absorbance of the sunflower oil. The scanned wavelengths were from 350 to 650 nm. The lowest absorbance curve at the bottom of this figure represents the unused oil. The curves from the second-lowest absorbance to the highest absorbance represent the oil samples taken from 1 to 10 d of deep frying (8 h/d), respectively.

set of oil samples. The equation for conversion of the spectrophotometric absorbance to TPC content is $y = -2.7865x^2 + 23.782x + 1.0309$ (Fig. 7). If 27% TPC is used as the maximal level allowed in the frying oil (2), the spectrophotometric absorbance of frying oil at 490 nm should be ≤1.3.

To further confirm the strong correlation between the absorbance and TPC, the 10 different types of oils with samples taken from 0 to 80 h of deep frying in duplicate were also tested using this method. The results showed that a strong correlation was also established ($r = 0.953$, $P < 0.001$, $n = 220$), and all data points were close to the fitted line (Fig. 8). It can be estimated from Figure 8 that if a 27% TPC limit is not to be exceeded in the frying oil, the absorbance at 490 nm should be ≤1.35. This value is similar to the value calculated from the calibration equation. This result shows that the spectrophotometric absorbance of frying oil is a good and reliable indicator of oil degradation for a variety of vegetable oils tested.

The principle of this method is based mainly on the measurement of the spectrophotometric absorbance of TPC in frying oil, such as free fatty acids, dimers, polymers, and other decomposition products. In order to demonstrate this, unused

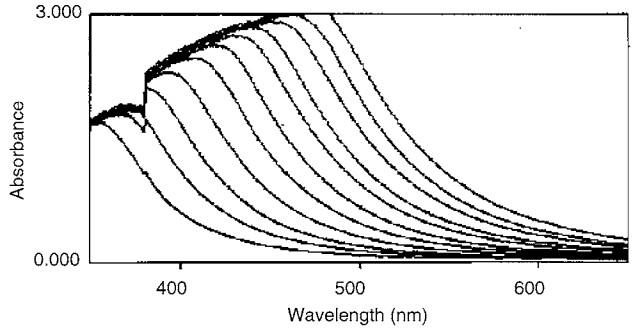

FIG. 4. Effect of frying time on absorbance of palm olein. The scanned wavelengths were from 350 to 650 nm. The lowest absorbance curve at the bottom of this figure represents the unused oil. The curves from the second-lowest absorbance to the highest absorbance represent the oil samples taken from 1 to 10 d of deep frying (8 h/d), respectively.

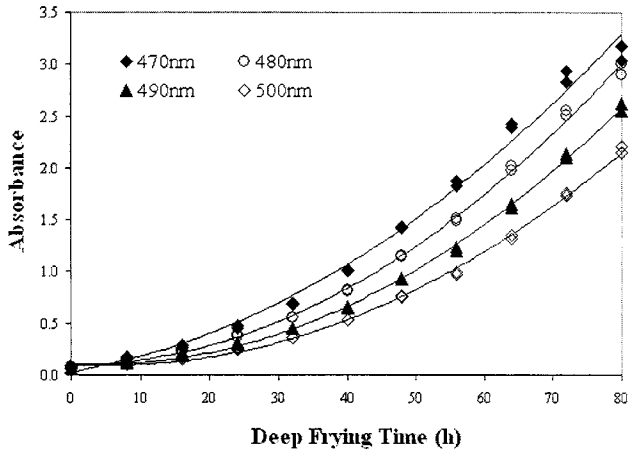

FIG. 5. Changes in spectrophotometric absorbances of the high-oleic canola oil containing 2.5% linolenic acid during deep frying (the two symbols at each data point in the graph represent the data taken from the two replicates).

high-oleic canola oil was mixed proportionally with polar compounds collected from the analysis of TPC in the frying oils using the AOCS method (8). The absorbances measured at 490 nm also increased proportionally with the TPC contents in the oil mixtures (Fig. 9). These polar compounds, eluted from the column using the standard method, were less colored, indicating that colored compound(s) also have an effect on the absorbance. This explains why, at the same concentration of 27% TPC, frying oil samples had higher absorbances than the fresh oil mixed with polar compounds collected from the column.

The 10 oils tested were four canola oils, a partially hydrogenated canola oil, a sunflower oil, two palm oleins, and two

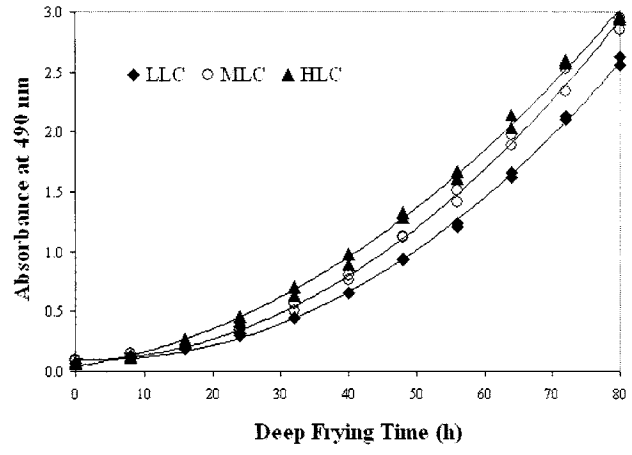

FIG. 6. Changes in spectrophotometric absorbances of the three high-oleic canola oils during deep frying. LLC, high-oleic canola oil containing 2.5% linolenic acid; MLC, high-oleic canola oil containing 4.4% linolenic acid; HLC, high-oleic canola oil containing 6.8% linolenic acid (the two symbols at each data point in the graph represent the data taken from the two replicates).

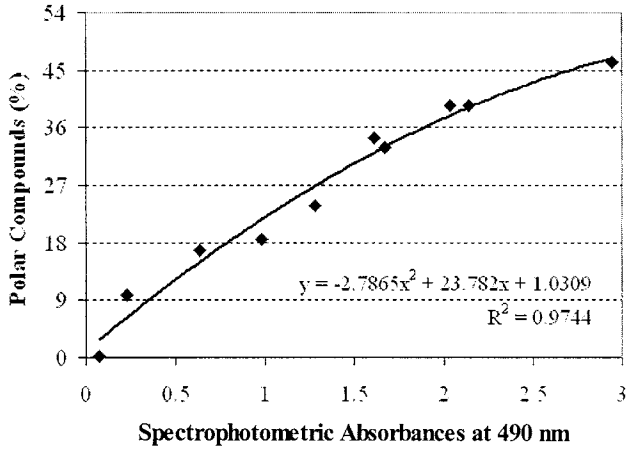

FIG. 7. Correlation of spectrophotometric absorbances at 490 nm and polar compounds determined using the American Oil Chemists' Society (AOCS) method (8) in a set of frying oils.

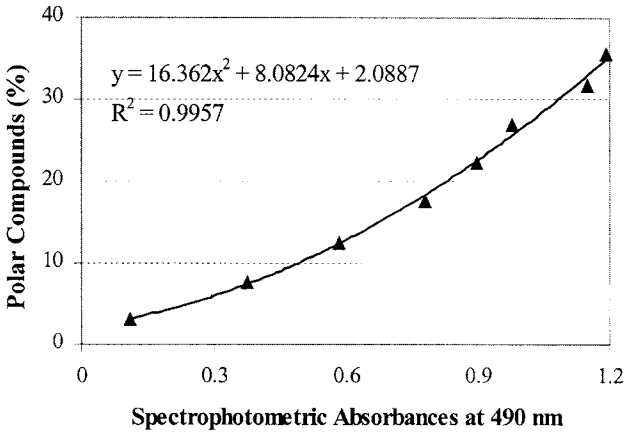

FIG. 9. Correlation of polar compound levels and absorbances at 490 nm. This graph shows that the absorbances at 490 nm increased proportionally to the levels of polar compounds in the samples when mixing known amounts of polar compounds collected from the analysis of total polar compounds using the AOCS method (8) with unused canola oil. For abbreviation see Figure 7.

palm–canola blends. There were 100 and 200 ppm of antioxidant (tertiary butylhydroquinone) in the two palm oleins, respectively, and 200 ppm of the antioxidant in the partially hydrogenated canola oil. In addition, there was 4 ppm of antifoaming agent in one of the palm oleins and the partially hydrogenated canola oil. The antioxidant and antifoaming agents appeared to have no notable effects on the absorbance, although they would be expected to reduce the rate of oxidation and the formation of decomposition compounds in the oils.

The type of food being fried in the oil may have an effect on the absorbance of the oil. In addition to TPC, other compounds accompanying various food products being fried in the oil may affect the absorbance of the oil. Further investigation with a variety of food products being fried in the oil may be necessary since only potato chips (French fries) were fried in the oils used in this study. If only one type of food is being fried in the oil and a good correlation between the absorbance and TPC determined by the standard method has been established, then the spectrophotometric absorbance measured at 490 nm can be used as a sole parameter for assessing frying oil quality. A frying oil with a spectrophotometric absorbance ≥1.35, as shown in this paper, should be discarded. The method is reliable, simple, fast and low cost, and can be used as a routine test for assessing frying oil quality.

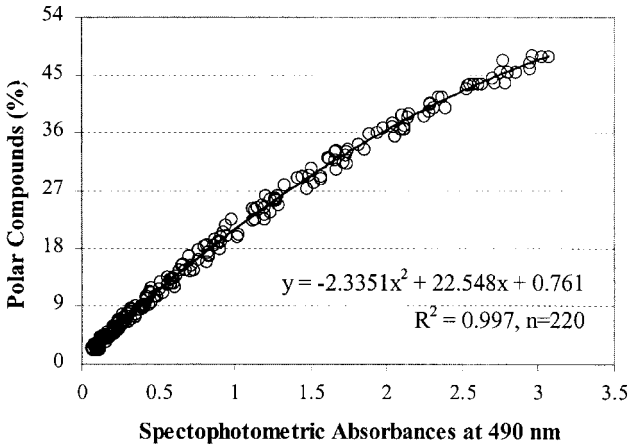

FIG. 8. Correlation of spectrophotometric absorbances at 490 nm and their corresponding contents of total polar compounds of the oil samples. The oil samples were taken from the 10 oils during 0 to 80 h of deep frying.

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