

FT-NIR Spectroscopy

Authors:

Hannah Rance

Rui Hua

Kathryn Lawson-Wood

PerkinElmer Inc.
Seer Green, UK

Determination of Peroxide Value (PV) and Acid Value (AV) in Fried Palm Oil Using Near-Infrared Spectroscopy and Multivariate Analysis

Introduction

Palm oil is an important and multipurpose vegetable oil with many uses in both food and non-food industries worldwide.¹

In 2017/18, 62.92 million tons of palm oil were consumed globally, accounting for 33.28% of total vegetable oil consumption.² It is, therefore, vital that the quality of palm oil produced meets health and safety regulations and customer expectations.

During the frying process, palm oil undergoes a series of degradation reactions, caused by heat, water and air, which results in oxidation of the oil and can ultimately reduce the quality of the oil and cause adverse health effects for consumers.³ The degradation products form in stages, starting with primary oxidation products, such as peroxides, and continually decomposing into secondary and tertiary products.⁴

The extent of oxidation in the oil can be assessed by determining the peroxide value (PV). Generally, the lower the PV, the higher the quality of the oil but very rancid oils, with high levels of oxidation, may have a reduced PV due to peroxides decomposing to form aldehydes and other secondary oxidation products. The acid value (AV) measures how many fatty acids have been cleaved from their parent molecule due to hydrolysis, which may result from the oxidation of the peroxides.⁴

The current and official methods for measuring these parameters involve manual titration as specified by the International Standards Organization. While being valid and reliable procedures, they can be time-consuming and labor intensive due to the essential preparation of specific reagents.⁵

Near-infrared (NIR) spectroscopy is already widely used in the food industry for quantitative analysis of nutritional and quality parameters. When combined with chemometric techniques, such as partial least squares (PLS), NIR spectroscopy can provide a simple, fast and accurate method for real-time monitoring of palm oil quality throughout the production process.

Experimental

274 fried palm oil samples, with known PVs and AVs, were collected from four industrial instant noodle fryers over a period of four months. During this time, the feed palm oil was changed on a regular basis. Before analyzing the samples, any noodle residues present were allowed to deposit and only an upper portion of the sample was used for analysis.

NIR spectra of the fried palm oil samples were collected using a PerkinElmer Spectrum Two NTM spectrometer with the PerkinElmer Heated Transmission Module (HTM), temperature controlled at 50 °C. Reference PVs and AVs for the samples were collected, in duplicate, using the current titration methods. The oxidation products liberate iodine from potassium iodide, and the amount of iodine formed is measured by titrating with sodium thiosulfate with a starch indicator.⁶ The acid components are titrated using KOH with phenolphthalein as an endpoint indicator.⁷



Figure 1. PerkinElmer Spectrum Two N with Heated Transmission Module

The samples were placed in 8 mm glass vials within the HTM, allowed to reach thermal equilibrium for three minutes and scanned using the parameters shown in Table 1.

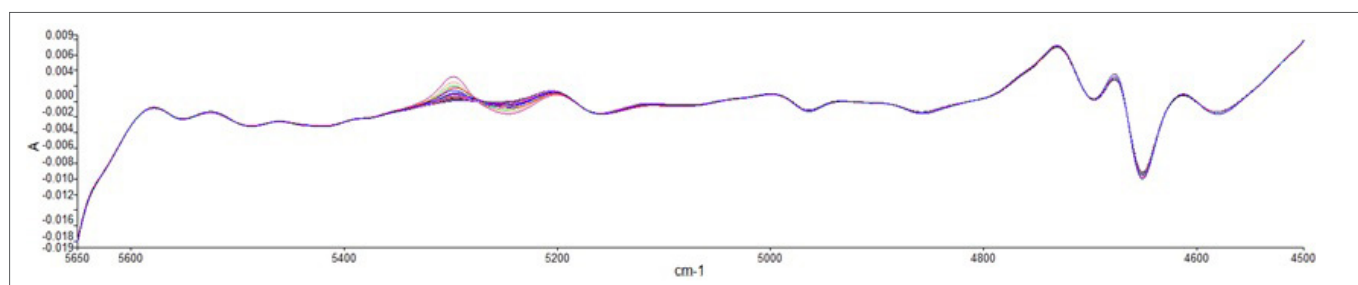


Figure 2. Pre-processed spectra for PV model, highlighting main region of spectral variations.

Table 1. Scanning parameters for the analysis of fried palm oil.

Scanning Parameters	
Spectral Range	10,000 - 4,000 cm ⁻¹
Resolution	8 cm ⁻¹
Number of Scans	32

All spectra collected were pre-processed using a first derivative baseline correction with light noise reduction. In the AV model, the spectral region 5,860 – 5,650 cm⁻¹ was excluded from all spectra as the absorbance values exceeded the upper absorbance threshold of 2.5. In the case of the PV calibration model, the spectral range was adjusted to include only the region 5,650 – 4,500 cm⁻¹ as this is the region showing most spectral variations, as seen in Figure 2. Raw and pre-processed fried palm oil spectra for the AV model are shown in Figure 3.

Partial Least Squares (PLS1) calibration models were built for PV and AV using PerkinElmer Spectrum QuantTM software. The samples were split such that 195 spectra were used to build the PV calibration model and 23 spectra were used for independent validation of the model. In the AV model, 226 spectra were used as calibration samples and independent validation was performed with the same 23 spectra used in the PV model.

Cross validation was carried out for all models. This was done using K-fold random cross-validation with 20 calibration sets for the PV model and K-fold sequential cross-validation with 10 calibration sets for the AV model.

Results and Discussion

Figure 4 illustrates correlation plots for each model, including both calibration and validation data points. The data points are distributed evenly around the unity line, showing there is a good level of agreement between reference measurements and analogous values determined using NIR.

The regression data for the calibration models is highlighted in Table 2. The R² values range between 93.9 – 94.9%, indicating a high level of correlation between the reference and predicted property values. Additionally, the standard errors of prediction (SEP) are relatively low.

Table 3 shows the average independent validation results for the models. There is an acceptable level of agreement between the predicted and reference values with a particularly good correlation for the AV model. In order to improve the model, a greater number of samples covering the whole calibration range could be taken. To improve the PV calibration model, more samples with higher PVs should be included.

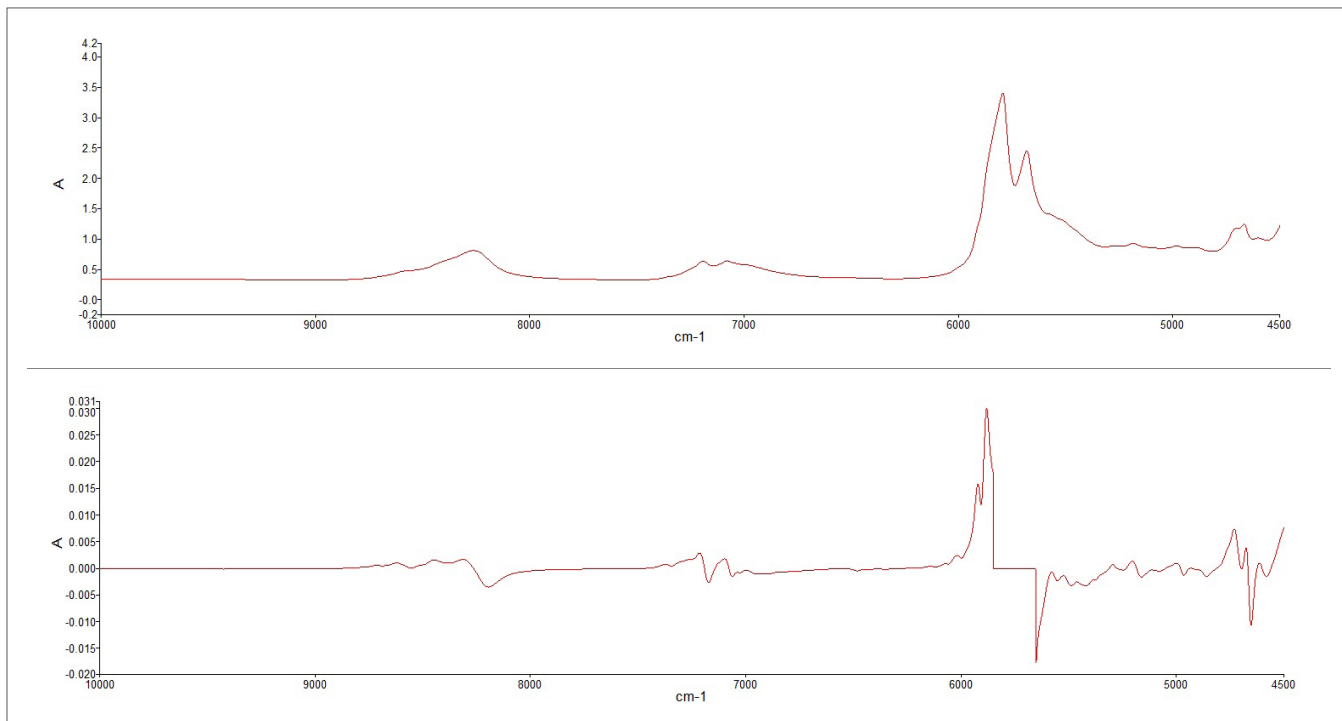


Figure 3. Example raw (top) and pre-processed (bottom) fried palm oil NIR spectra for the AV model.

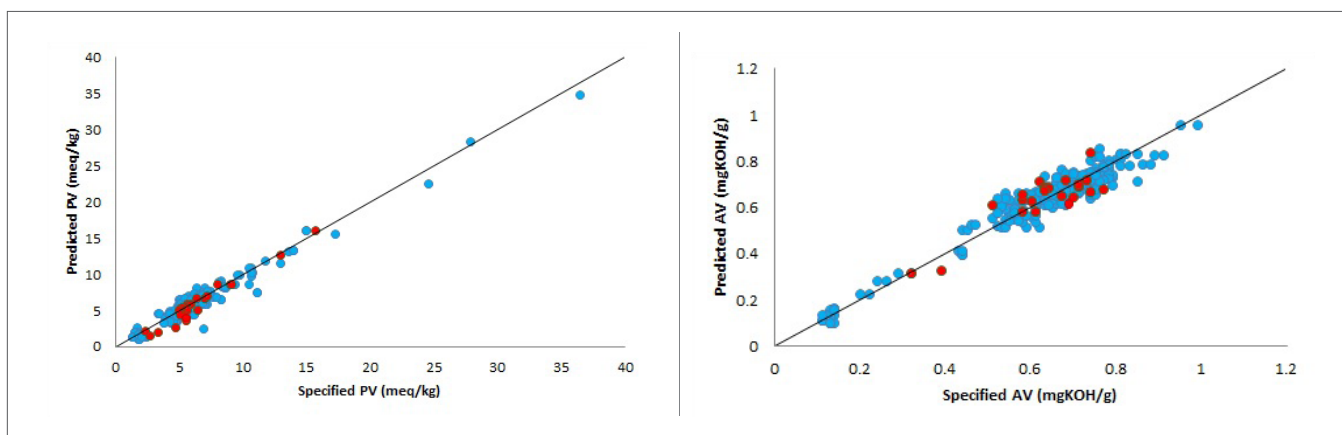


Figure 4. Correlation plots for PV model (left) and AV model (right) showing calibration (blue) and validation (red) data points with the solid black line indicating the unity line.

Table 2. Regression summary for PV and AV models (where SEC is the standard error of calibration, SEP is the standard error of prediction, and CVSEP is the cross validation standard error of prediction).

Property	Average Property Value (Range)	Number of Calibration Spectra	Number of Validation Spectra	Number of PCs	R ²	SEC	SEP	CVSEP
PV (meq/kg)	6.385	195	23	8	94.909	0.914	0.938	1.212
AV (mgKOH/g)	0.626	251	23	9	93.873	0.045	0.046	0.058

Table 3. Independent validation results for POV and AV models.

Model	Average True Sample Property Value	Average Predicted Sample Property Value	SEP
PV (meq/kg)	6.41	6.06	0.819
AV (mgKOH/g)	0.63	0.64	0.060

Fried Palm Oil Quality Check Using Spectrum Touch Software

The PV and AV of fried palm oil can be determined rapidly and simply using PerkinElmer's Spectrum Touch software. The method consists of step-by-step instructions with a user-friendly interface, as shown in Figure 5. This allows routine operators to check the quality of the oil samples, without the need to spend time and money on extensive training.

The calibration models are incorporated directly into the Touch method so the user simply needs to follow the instructions and scan the samples for analysis. The user can change the sample table before analysis in order to scan as many or as few samples as necessary.



Figure 5. Spectrum Touch Workflow example for fried palm oil quality check.

Conclusion

Near-infrared spectroscopy with a Heated Transmission Module provides a rapid, environmentally friendly, and non-destructive technique for analysing the extent of oxidation within fried palm oil samples. In contrast with the traditional titration methods for PV and AV determination, the Spectrum Two N requires no chemical reagents and the operating time is reduced tenfold. The PerkinElmer Spectrum Two N is also transportable, allowing analysis to be carried out on the production line. Furthermore, Spectrum Quant methods can be incorporated into Spectrum Touch software to produce simple, user-friendly workflows in order to quantify the PV and AV of a fried palm oil sample.

References

1. G. Pande, C. C. Akoh and O. Lai, *Food Uses of Palm Oil and Its Components*, Palm Oil, 2012, 561-586.
2. *Consumption of vegetable oils worldwide from 2013/14 to 2017/18*, Statista, 2018.
3. R. Wannahari and M. F. N. Nordin, *Reduction of Peroxide Value in Used Palm Cooking Oil Using Bagasse Adsorbent*, American International Journal of Contemporary Research, 2012, 2, 185-191.
4. M. Miller, *Oxidation of food grade oils*, Plant and Food Research, 2016.
5. C. W. Kwon, K. Park, J. W. Park, J. Lee, S. J. Choi and P. Chang, *Rapid and Sensitive Determination of Lipid Oxidation Using the Reagent Kit Based on Spectrophotometry*, Journal of Chemistry, 2016, 2016.
6. F. Kong and R. P. Singh, *Advances in instrumental methods to determine food quality deterioration*, Food and Beverage Stability and Shelf Life, 2011, 381-404.
7. E. Kardash and Y. I. Tur'yan, *Acid Value Determination in Vegetable Oils by Indirect Titration in Aqueous-alcohol media*, Croatica Chemica Acta, 2005, 78, 99-103.