

FT-NIR Spectroscopy

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Determination of Quality Parameters of Crude Palm Oil using Near-Infrared Spectroscopy and Multivariate Analysis

Introduction

Edible oils are an integral part of human diets; being used in virtually all types of culinary practices. The edible oils global market is expected to exceed 200 million metric tons by 2020, with palm oil projected to take

a one third share. Simple analysis of oil quality is essential to maintain process efficiency, and minimise costs associated with high chemical usage and waste treatment.¹

Crude palm oil (CPO) is obtained from the fibrous mesocarp (reddish pulp) of palm fruit. The oil itself is semi-solid and reddish-orange in color owing to the presence of carotene (pro-vitamin A).² Various parameters are used to assess its quality, including iodine value (IV), moisture and free fatty acid (FFA) content. Traditional methods of analysis are typically carried out using standardized methods approved by the American Oil Chemists' Society (AOCS), the German Society for Fat Science (DGF) and the Malaysian Palm Oil Board (MPOB). However, these methods usually determine only one particular parameter and analysis is often time-consuming. Additionally, sample preparation can be extensive, with hazardous solvents and reagents being required.³

Near-infrared (NIR) spectroscopy is an already widely used technique in the food industry for quantitative analysis of nutritional and quality parameters. Chemometric techniques, such as partial least squares (PLS), used in conjunction with NIR spectroscopy offers an alternative rapid and non-destructive method to the wet chemistry reference methods for the analysis of CPO, with multiple property values being determined simultaneously.

Palm Oil Quality Parameters

Free Fatty Acids (% FFA), also commonly referred to as acidity, is a measure of the quality as poor storage of the oil will cause hydrolysis, thereby increasing acidity levels. The % FFA wet chemical test determines the amount of potassium hydroxide (mg) required to neutralise the fatty acid in 1 g of palm oil, through titration. The Palm Oil Refiners Association of Malaysia set a maximum level of free fatty acids content in CPO of 5 %.²

Moisture (%) in oils can cause rancidity and levels can range from 0.05 – 0.30 % without any physical evidence of its presence. Analysis is traditionally carried out in several different ways, including determining the loss in mass undergone by the product on heating (hot-plate, vacuum oven, or air oven methods), or by use of the Karl Fischer method. The latter method is quicker and eliminates the need for heat but uses environmentally hazardous chemicals such as sulfur dioxide, pyridine and chloroform.⁴

Iodine value (IV), typically determined by the Wijs Method, is a measure of the degree of unsaturation or double bonds in fats and oils and is expressed in terms of the amount of iodine (g) reacted per 100 g of sample. A higher IV indicates a greater degree of unsaturation, and thus lower oxidative stability. During oxidation of oils, low-molecular weight off-flavor compounds are produced, affecting both oil quality and shelf life.^{5,6}

Experimental

Near-IR spectra of 203 crude palm oils with known IV, FFA (%) and moisture (%) content were collected in transmission mode using a PerkinElmer Frontier™ FT-IR/NIR spectrometer with a Pike Falcon NIR transmission accessory, temperature-controlled at 65 °C (Figure 1). Although the Frontier was used in this particular application, the PerkinElmer Spectrum Two N FT-NIR spectrometer may also be used. The Frontier FT-IR/NIR benefits from high end performance and a large spectral range which can be especially useful for different edible oil applications. The Spectrum Two N on the other hand has high end performance but is portable, allowing samples to be analyzed anywhere, for example in a production facility.

Reference IV and FFA values were determined using MPOB methods c2.6:2014 and c2.7:2014, respectively. Karl Fischer titration was used in determining moisture reference values. Absolute virtual instrument (AVI) technology was applied during scanning to reduce inconsistencies in wavenumber calibration and instrument line shape across multiple instruments. Samples were pipetted into disposable glass vials following heating, placed into the heated transmission accessory and left for one minute before scanning to reach thermal equilibrium. The disposable glass vials had inner and out diameters of 10 mm and 12 mm respectively. Scanning parameters are illustrated in Table 1.

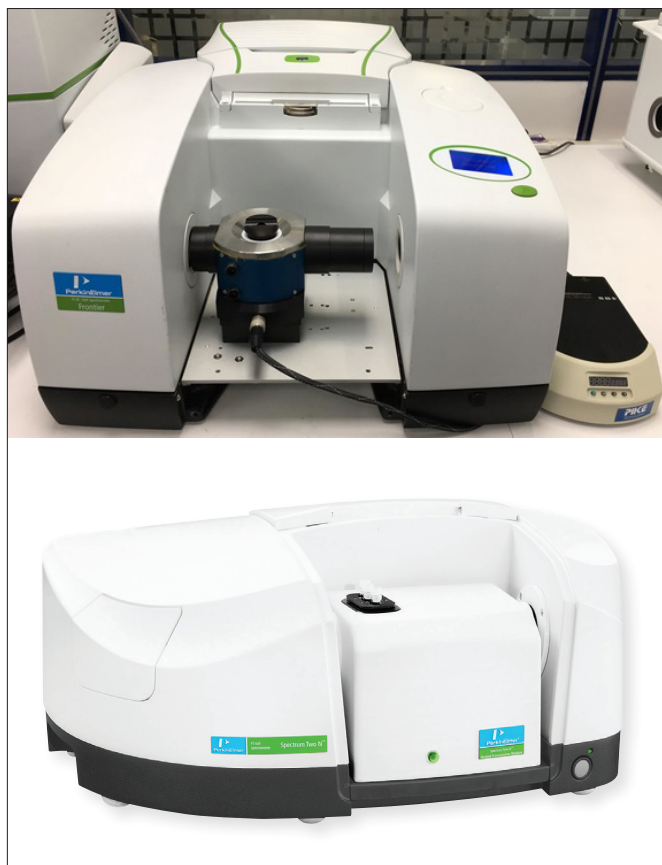


Figure 1. Alternative instrument setups. Top) PerkinElmer Frontier FT-IR/NIR with Pike Falcon NIR transmission accessory. Bottom) PerkinElmer Spectrum Two N with Heatable Transmission Module (HTM).

Table 1. Scanning parameters for the analysis of CPO.

Scanning Parameters	
Spectral Range	8,300 – 4,500 cm^{-1}
Resolution	4 cm^{-1}
Number of scans	8

All spectra were pre-processed using baseline offset correction, an upper absorbance limit of 2.5 absorbance units, and the spectral range adjusted to 7,500 - 4,500 cm^{-1} . Partial Least Squares (PLS1) calibration models were built for FFA, IV, and moisture using PerkinElmer Spectrum Quant™ software. The overall CPO dataset was randomly split into calibration and validation datasets in which 80 % of spectra were used for building the calibration model and the remaining 20 % used for independent validation. Cross validation was performed using K-fold sequential cross-validation omitting 10 % of the calibration dataset.

Results and Discussion

Raw and pre-processed CPO spectra are shown in Figure 2. PLS models were independently optimized for each property value of interest. Table 2 highlights regression details for the final calibration models. R-squared values range from 88 - 98 % indicating good correlation between reference and predicted property values. Correlation plots including both calibration and validation data points are shown in Figure 3 for FFA, IV, and moisture. In all cases, data points are randomly distributed about the unity line indicating good agreement between reference measurements and analogous values determined using NIR.

The FFA, moisture and IV models were validated using approximately 20 % of the sample data, randomly selected and spanning the concentration ranges of the calibration models. Table 3 shows the average validation results for each model, demonstrating good agreement between predicted and reference values. Model performance can be further improved by including a greater number of samples spanning the entire calibration range. In the case of the IV calibration, a greater number of samples with lower IVs would help improve the model.

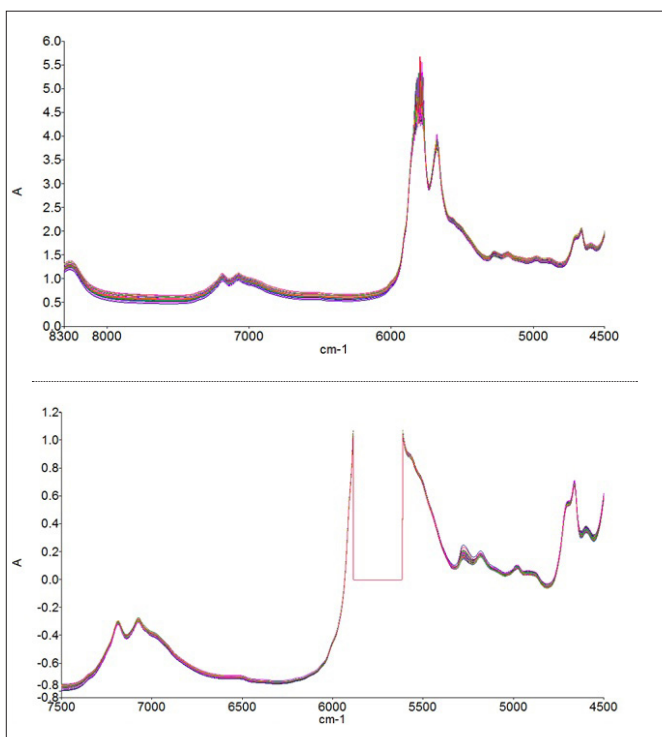


Figure 2. Example raw (left) and pre-processed (right) CPO NIR spectra.

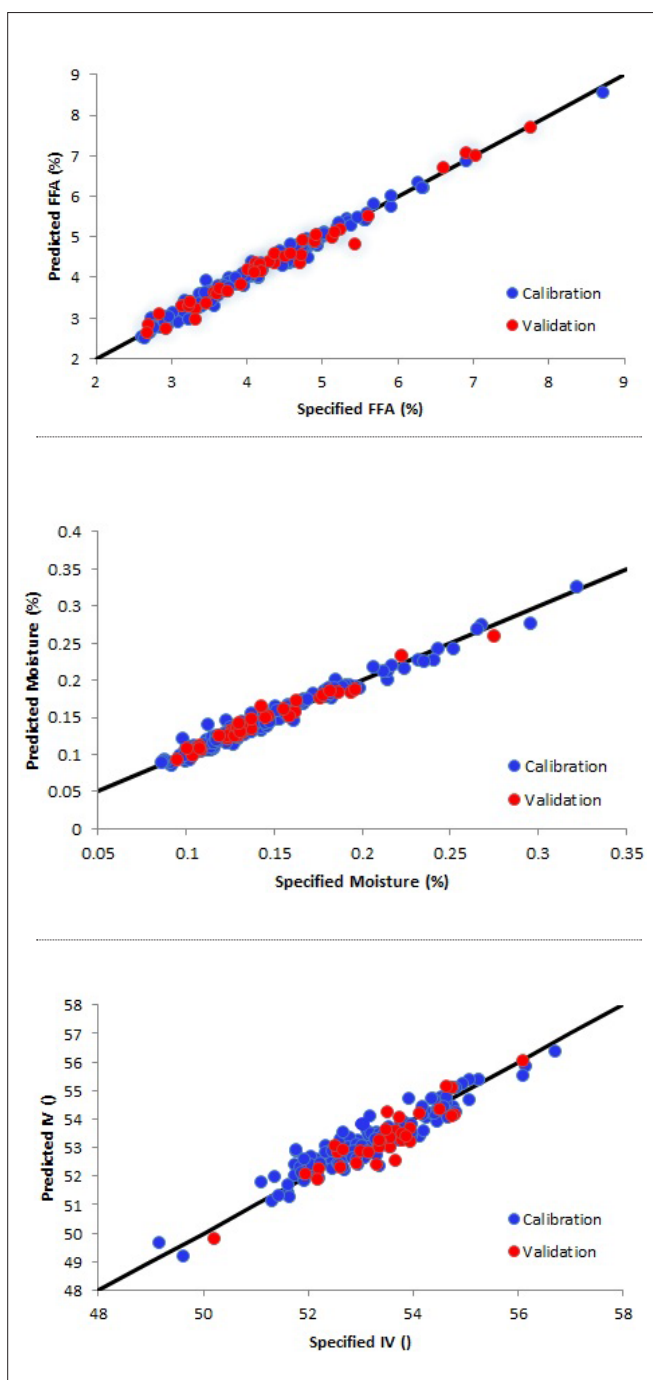


Figure 3. Correlation plots for FFA (top), moisture (middle), and IV (bottom) showing calibration (blue) and validation (red) data points with the black solid line indicating the unity line.

Table 2. Regression summary for FFA, moisture and IV PLS 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
FFA (%)	4.22 (2.61 – 8.72)	163	40	5	98.332	0.121	0.127	0.135
Moisture (%)	0.14 (0.09 – 0.33)	153	37	3	97.223	0.007	0.008	0.008
IV	53.23 (49.18 – 56.71)	137	34	5	88.788	0.397	0.410	0.415

Table 3. Independent validation results for FFA, moisture and IV models.

Model	Average True Sample Property Value	Average Predicted Sample Property Value	SEP
FFA (%)	4.38	4.37	0.160
Moisture (%)	0.15	0.15	0.007
IV	53.46	53.27	0.455

Simplifying the Measurement Process Using PerkinElmer's Spectrum Touch™ Software

Quantitative results can be achieved using a Spectrum Touch method specifically designed to perform CPO analysis. Spectrum Touch methods are aimed at routine operators to achieve rapid results and encompass a simple interface with step-by-step instructions, as shown in Figure 4. This eliminates the need for costly and time-consuming training. Calibration files are incorporated directly into the Touch method and the user simply follows the sample preparation steps in the guided Spectrum Touch workflow.

An example of the results output created from a Spectrum Touch workflow for the analysis of a CPO sample using the PLS methods is shown in Figure 5.

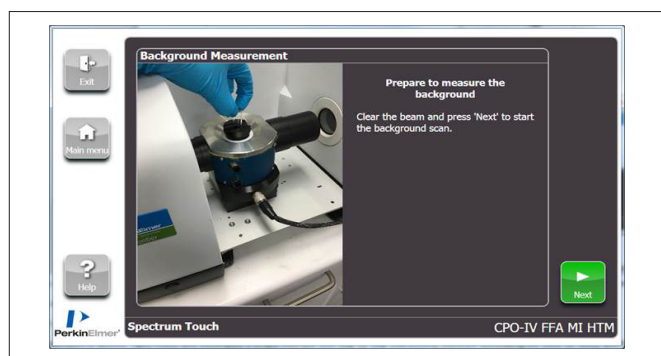


Figure 4. Spectrum Touch workflow example for CPO analysis.

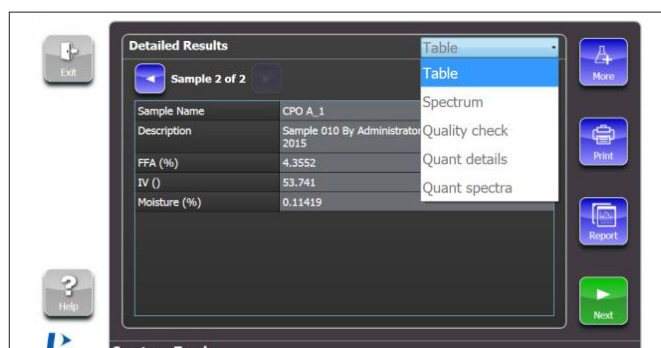


Figure 5. Spectrum Touch results output example from the analysis of a CPO sample. Further results may be found in the drop-down list.

Conclusion

Near-infrared spectroscopy with transmission mode sampling provides a rapid (<one minute), environmentally friendly, and non-destructive alternative to the wet chemistry reference methods for quality analysis of downstream palm-oil based end products. The PerkinElmer Frontier FT-IR system demonstrates good accuracy in determining % FFA, moisture (%), and IV of CPO and can provide multiple parameter results simultaneously, allowing for higher sample throughput. Advancements in technology also means NIR instrumentation for edible oils analysis can be portable, as such with the PerkinElmer Spectrum Two N with the Heatable Transmission Module. Additionally, Spectrum Quant methods may be implemented into Spectrum Touch software in order to achieve a simple, workflow based approach to the quantitation of palm oil quality parameters.

References

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