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APPLICATION OF NIR SPECTROMETER FOR OIL LOSS MONITORING IN PALM OIL MILL

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ABSTRACT

A faster determination method for oil content in the samples of pressed fibre, sludge, steriliser condensate and empty fruit bunches in palm oil mill processing points is needed to monitor and control the oil loss so that the oil extraction rate (OER) could be increased. The spectroscopic method is based on molecular overtone and combination vibration bands which are typically very broad in the near infrared (NIR) region that produces spectra that are too complex for direct interpretation of the oil content in biomass components. Now with the progress made by computer aided NIR technology, it has become possible to conduct complex analysis of the data captured by the NIR spectrometer. The objective of this study is to generate a series of calibration curves for the residual oil content in press fibre, palm oil sludge, steriliser condensate and empty fruit bunches, using direct laboratory analytical data as the reference data. These curves can be used by the industry with measurable level of accuracy to analyse the oil loss in the biomass component to help the millers to implement corrective action immediately to control oil losses.

Keywords: NIR spectrometer, calibration curve, oil loss monitoring.

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INTRODUCTION

Malaysian Palm Oil Board (MPOB) as well as large plantation companies have established standard oil content analysis method for samples taken from various sampling points involving time consuming sample pre-treatment procedures using hexane soxtec or soxhlet extraction as shown in *Figure 1* (Ainie Kuntom *et al.*, 2005). Even though these test methods produce accurate and reliable results, the results are available only after one day during which time if there are any high losses in any of the areas it would continue without any check using the present system. The industry has been eager to get an on-line analytical system that would allow it to enforce corrective action in time as soon as the losses are detected. This is expected to raise national OER by controlling process loss.

The current advancement of near infrared (NIR) technology appears to effectively fill the vacuum on oil loss control. Recently, successful performance using NIR spectrometer (MPOB, 2011) has been reported. NIR spectroscopy is a fast analytical technique using waves in the NIR region of the electromagnetic spectrum having wavelength ranging from 800 nm to 2500 nm. No sample preparation is needed and the technique is non-destructive. If samples contain such bonds as CH, NH or OH with concentrations exceeding about 0.1% of total composition, the results are reliable and acceptable. Signals in the NIR spectra of chemical compounds can be observed as a consequence of molecular vibrations, and NIR spectroscopy is based on the absorption of radiation. The molecular overtone and combination bands seen in the NIR are very broad leading to complex spectra (Roman *et al.*, 2007). Modern NIR technology relies heavily on the computer to control and acquire data from the instrument and facilitate calibration and data analysis (Burns and Ciurczak, 2008).

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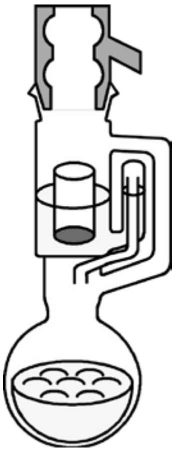

	Preparation time (hr)	
Sample preparation process	**Solid sample**	**Liquid sample**
Preparation	0.5	0.5
Drying	6	10
Cooling & weigh	1.5	1.5
Solvent extraction	6	6
Solvent removal drying	2	2
Cooling & weigh	1	1
Total time	17	21

Figure 1. Soxtec or soxhlet extraction method and estimated time needed.

NIR Spectroscopy

Types of electromagnetic radiation is shown in *Figure 2*. The discovery of NIR energy is ascribed to Herschel in the 19th century, but the first industrial application began in the 1950s. NIR methods of analysis were first developed by the United States Department of Agriculture (USDA) in the mid 1960s to detect the internal qualities of apple. A stand-alone near infrared spectroscopy (NIRS) system focusing more on chemical analysis was made available in the 1980s. It then became a more powerful tool for scientific research due to the introduction of light fibre optics in the mid 1980s and the mono chromator detector developments in the early 1990s. It is only in the last few decades that NIRS began to be used as a medical tool for monitoring patients.

NIR spectroscopy is not a particularly sensitive technique but can be very useful in probing bulk material with little or no sample preparation. The spectroscopic method is based on molecular overtone and combination vibration bands which are typically very broad in the NIR leading to complex spectra and thus making it difficult to analyse. Application of multivariate calibration techniques to develop a set of calibration samples is essential for NIR analytical methods (Mehta, 2011).

NIR spectroscopy instrumentation consists of a source usually broadband light emitting diodes; incandescent light bulbs or quartz halogen light bulbs; a detector, such as silicon-based charge coupled device (CCD) or indium gallium arsenide (InGaA) and lead sulphide (PbS), depending on the range of wavelengths to be measured; and a dispersion element, such as a prism or diffraction grating, to allow the intensity at different wavelengths to be recorded. Fourier transforms of NIR instrument signals with wavelengths above 1000 nm are used in an interferometer. The spectrum can be measured in either reflection or transmission depending on the sample. Instruments intended for chemical imaging in the NIR may use a 2D array detector with an acousto optic filter. Multiple images may be recorded sequentially at different narrow wavelength bands (Bakshi and Godse, 2009).

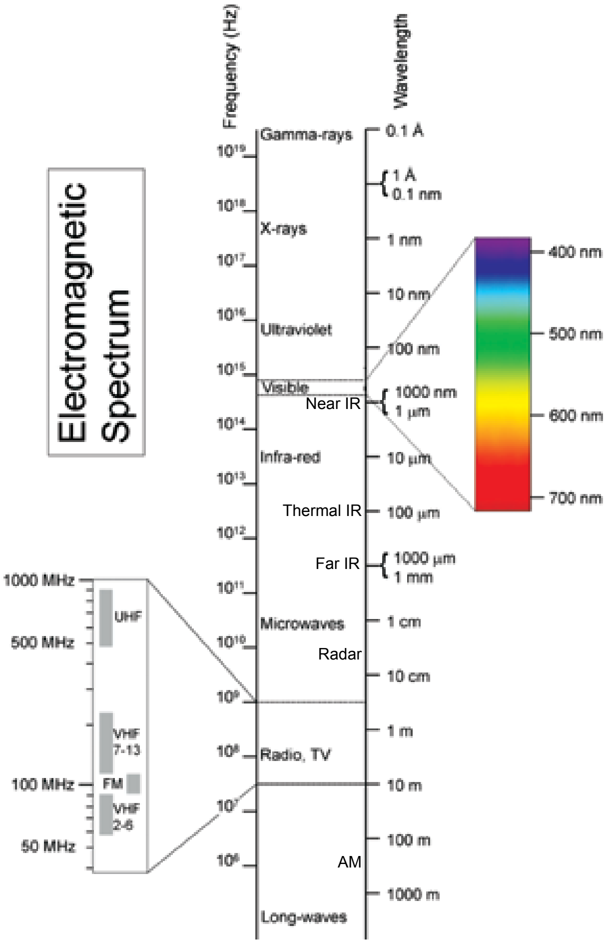

Figure 2. Types of electromagnetic radiation.

Absorption Principles of NIR Spectroscopy

In a harmonic diatomic oscillator model with less than 10% change of the inter nuclear distance, from Hooke's Law the potential energy,

$$V = 0.5kq^2 \tag{1}$$

where k is the force constant of the bond and q is the displacement coordinate of the inter nuclear distance. The potential energy curve of oscillator above is a symmetrical parabola at equilibrium bond length. Thus, the vibration frequency

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{m}}\ ;\ m = \frac{m_1 m_2}{m_1 + m_2} \tag{2}$$

where m_1 and m_2 are the vibrating masses. Equation (2) elucidates the vibration frequencies as very sensitive to the compound structure which form the basis of the infrared spectroscopy application. Schrödinger's quantum mechanic equation shows that the vibration energy, E has only certain discrete values given by

$$E = hv\ (n + 0.5) \tag{3}$$

where h is Planck's constant and n is the integer vibration quantum number. At larger amplitudes of vibration, the harmonic oscillator cannot be retained due to the repulsive forces between the vibrating atoms and the possibility of dissociation when the vibrating bond is strongly extended. Thus, the energy levels for enharmonic oscillator, G is

$$G = u(n + 0.5) - \chi u(n + 0.5)^2\ ;\ u = \frac{1}{2c\pi}\sqrt{\frac{k}{m}} \tag{4}$$

where c is the speed of light, u is the wave number corresponding to the frequency v and χ is the enharmonic constant. Vibration degree of freedom for molecule with N_a atoms is $3N_a$-6 for non-linear while linear has $3N_a$-5. The vibration degree of freedom represents the number of different normal modes of vibration for a given molecule. A normal mode of vibration corresponds to internal atomic motions in phase with the same frequency but with different amplitudes. Overtones are the transition number of these normal vibrations.

NIR absorption bands which are very broad, highly overlapped but weaker than IR spectrum allow direct analysis of strongly absorbing, highly light scattering matrices such as slurries, suspensions, pastes and powders. NIR spectroscopy offers a wide range of in-line, on-line and at-line transmission and diffuse-reflection probes designed for large sample volume measurement of liquid and solid (Burns and Ciurczak, 2008).

OBJECTIVE

The objective of this study is to carry out calibration of NIR spectrometer to generate standard curves on samples of press fibre, sludge, steriliser condensate and empty fruit bunches so that oil loss in the respective sample could be determined much faster than the current standard method of analysis.

METHODOLOGY

The FOSS InfraXact 7500 NIR spectrometer equipped with ISIScan 4.2.0 and WinISI III Version 1.60 software was installed in Sime Darby R&D Palm Laboratory, Carey Island, Klang, Selangor, Malaysia. Samples were taken hourly from the respective sampling points of a nearby palm oil mill during the mill operation according to the Protocol for Measuring Oil Losses (Zulkifli *et al.*, 2010) and analysed with NIR spectrometer. The respective sample was then analysed in laboratory according to the MPOB Test Method. Graph of laboratory reading versus NIR spectrometer was plotted for each sampling point. Statistical analysis was performed using WinISI III software to determine the accuracy and the level of confidence for each calibration curve.

FOSS Infraxact 7500 NIR spectra was acquired as an average of 32 scans between 570 and 1850 nm, with 32 scans using air as background. Wavelength increments of 2 nm were used. The sample data were recorded as log (R^{-1}) where R is the reflectance energy. A sample was replicated 10 times to determine the mean and standard deviation (SD) at each wavelength and then summed to determine the replicate instrumental error in NIR predictions. Diagnostic test for wavelength (0.5±0.002 nm) were performed daily before samples were scanned.

Principal component analysis (PCA) was used to evaluate the respective samples spectra, then subjected to various mathematical processing treatments such as standard normal variant (SNV) transformation and de-trend scatter correction (*D*) which removed or reduced linear and quadratic curvature of each spectrum. Calibration performance is based on the statistics such as standard error of calibration (SEC), standard error of cross-validation (SECV) and coefficient of determination (R^2).

RESULTS

Four NIR calibration models for oil and moisture content in pressed fibre, sludge, empty fruit bunch and steriliser condensate respectively were duly established as shown in *Table 1, Figures 3, 4, 5, 6, 7, 8, 9* and *10*.

DISCUSSION

NIR absorption bands occurring at longer wavelengths are stronger, sharper and better resolved than their corresponding higher overtone bands occurring at shorter wavelengths. The optimal spectral region to be used for a particular analysis is determined by matching the spectral properties of the NIR region with the required analytical performance, the sampling requirements and the physical properties of the sample because in the NIR spectral region, light scattering efficiency and absorptivity increase with wavelength whereas band overlap and penetration depth decrease with wavelength.

Generally, NIR spectra on translucent samples are performed in transmittance mode whereas NIR spectra on opaque or light scattering matrices are performed in diffuse reflectance mode. It is often difficult to identify unique spectral features related to individual chemical components within a given matrix for both measurement modes. Thus, a mathematical pre-treatment is applied to the spectral data of NIR spectroscopy to enhance spectral features and compensate for baseline offsets. Usually the second derivative of the absorbance data with respect to wavelength is calculated and the absorbance maximals are converted to minima with positive side-lobes. The apparent spectral bandwidth is sharply reduced to enable for overlapping peaks resolution and eliminate baseline differences between spectra.

Spectral library matching or pattern recognition algorithms are used to perform qualitative NIR analysis. The NIR spectrum of an unknown material is compared to the composite spectra for all materials with the spectral variance determined for each of the acceptable materials contained within a library. Positive and negative control samples are used to validate the derived spectral library. Wavelength Correlation or statistical methods such as Mahalanobis distance or residual variance methods are employed to derive a correlation value.

Since interfering absorption bands due to other components and matrix variations can affect the spectroscopic measurements, empirical relationships between the NIR spectra for a set of calibration samples and the corresponding reference analytical method for the interest constituents are derived in quantitative NIR spectroscopy. The calibration set of samples should be representative of the variation in the sample properties to be encountered in typical production lots to ensure representative quantitative results are obtained.

An algorithm such as multiple linear least-squares regression (MLR), partial least-squares (PLS) and principal component regression (PCR) analysis is used to derive the NIR spectroscopic models. MLR is usually reserved for simple chemical systems, derives linear relationships between the absorption of NIR energy at discrete wavelengths and the reference analytical chemistry for specific constituents. The primary wavelength is related to the interest constituents. Subsequent wavelengths can be included to compensate for

TABLE 1. SUMMARY OF CALIBRATION DEVELOPED USING INFRAXACT 7500

Product name	Sample No.	Parameters	Range		R^2	SEC	SECV	SEP
			Min	Max				
Pressed Fibre	172	Oil	0.56	6.39	0.923	0.275	0.314	0.28
	165	Moisture	26.13	55.57	0.930	1.339	1.509	3.00
Condensate	165	Oil	0.14	0.76	0.985	0.020	0.030	0.03
	163	Moisture	94.44	97.18	0.993	0.069	0.104	0.047
Sludge	169	Oil	0.43	1.51	0.969	0.032	0.056	0.062
	185	Moisture	91.99	96.48	0.993	0.064	0.117	0.14
EFB	153	Oil	0.24	5.50	0.874	0.470	0.521	0.44
	154	Moisture	10.52	87.46	0.924	3.933	4.915	5.50

Note: SEC - Standard error of calibration.
SEP - Standard error of prediction.
SECV - Standard error of cross-validation.
R^2 - Coefficient of determination.
EFB - Empty fruit bunch.

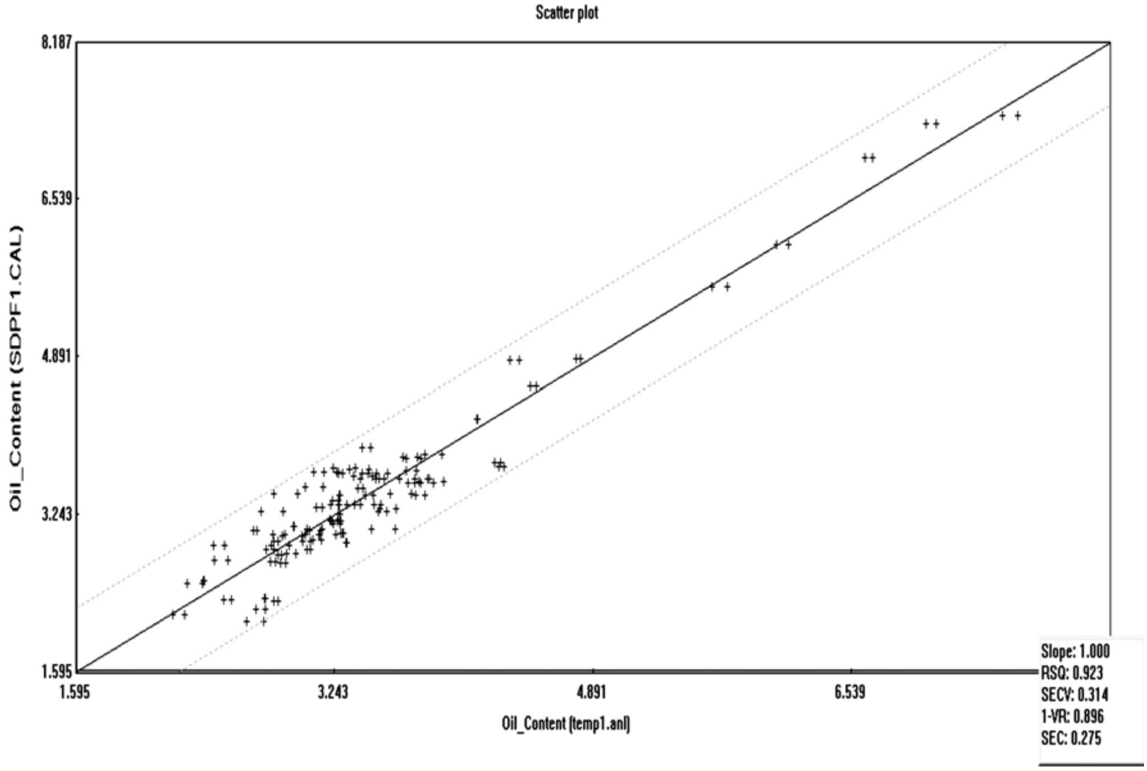

Figure 3. Near infrared (NIR) calibration curves for oil content in pressed fibre.

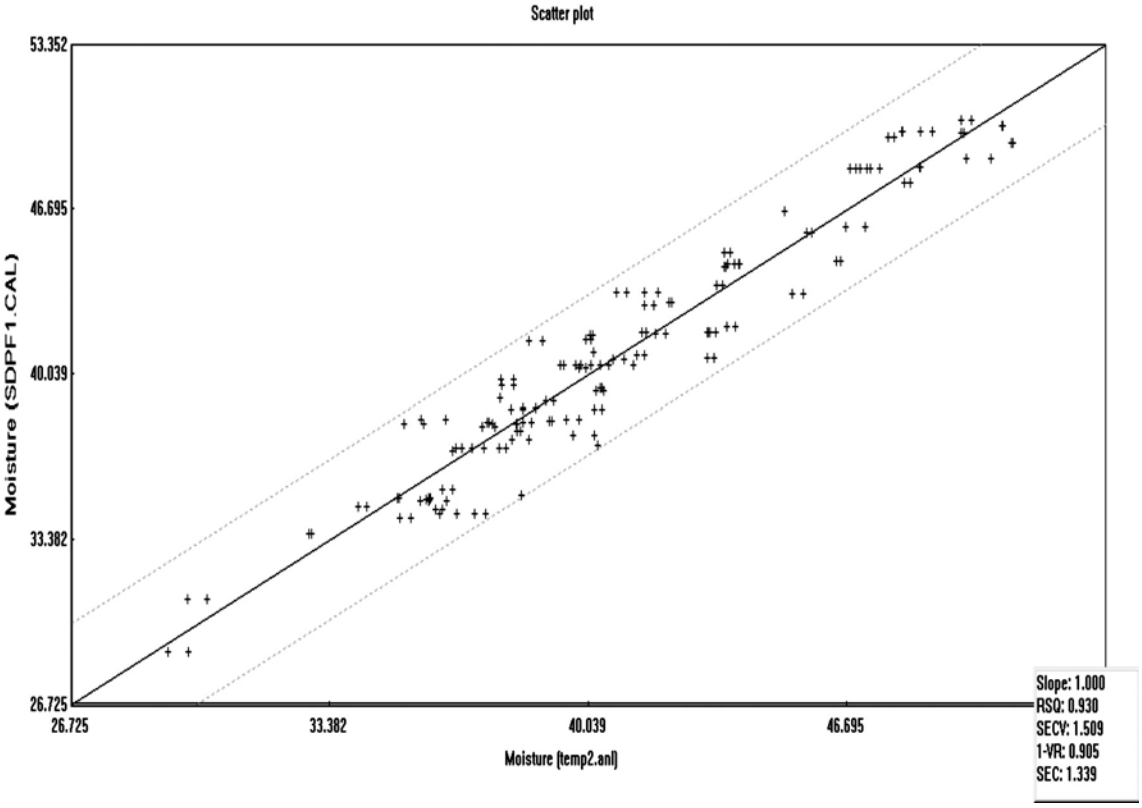

Figure 4. Near infrared (NIR) calibration curves for moisture in pressed fibre.

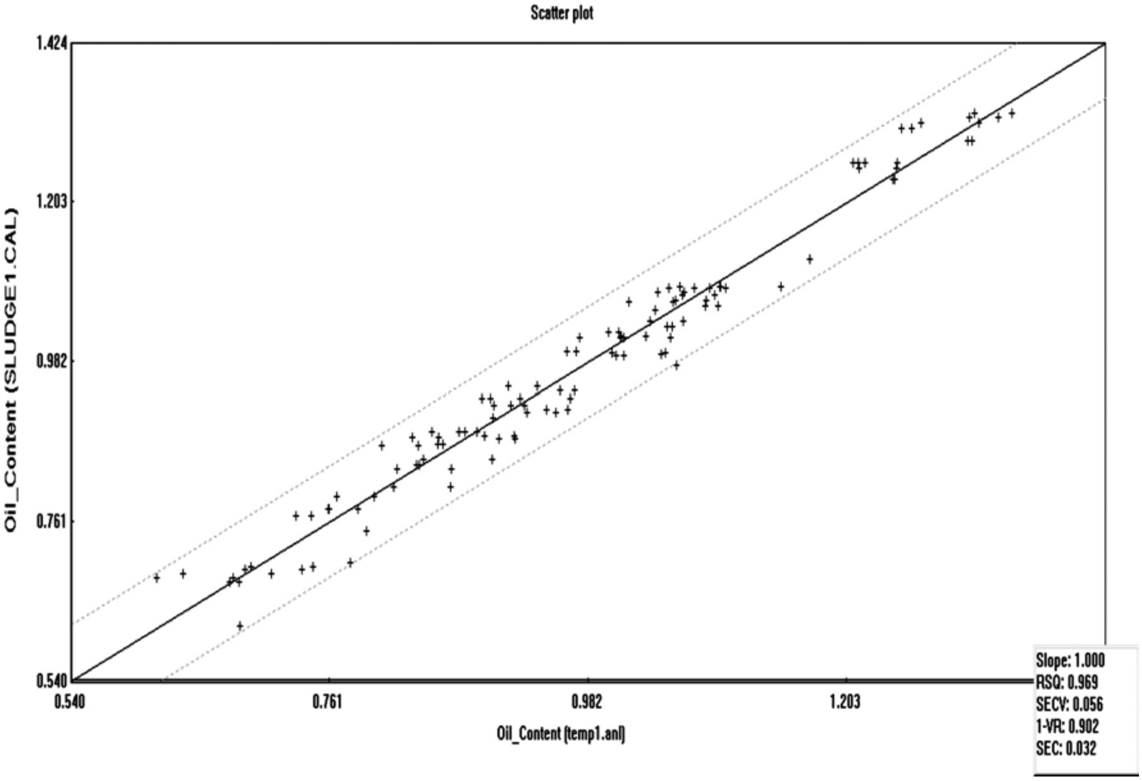

Figure 5. Near infrared (NIR) calibration curves for oil content in sludge.

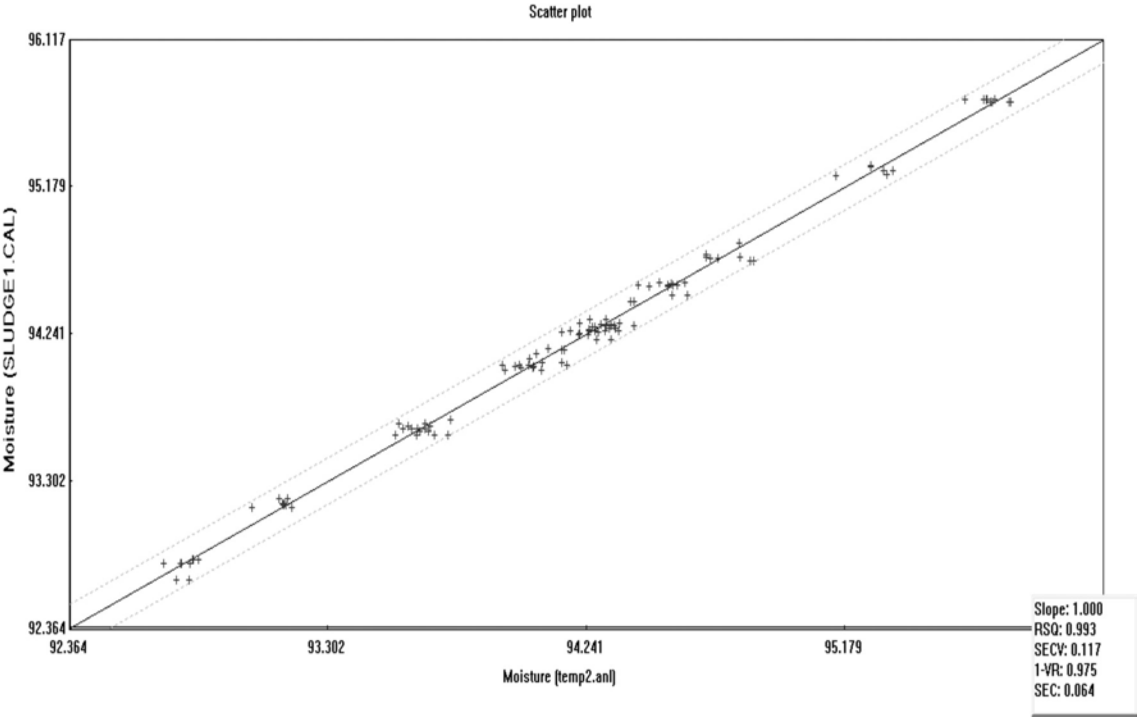

Figure 6. Near infrared (NIR) calibration curves for moisture in sludge.

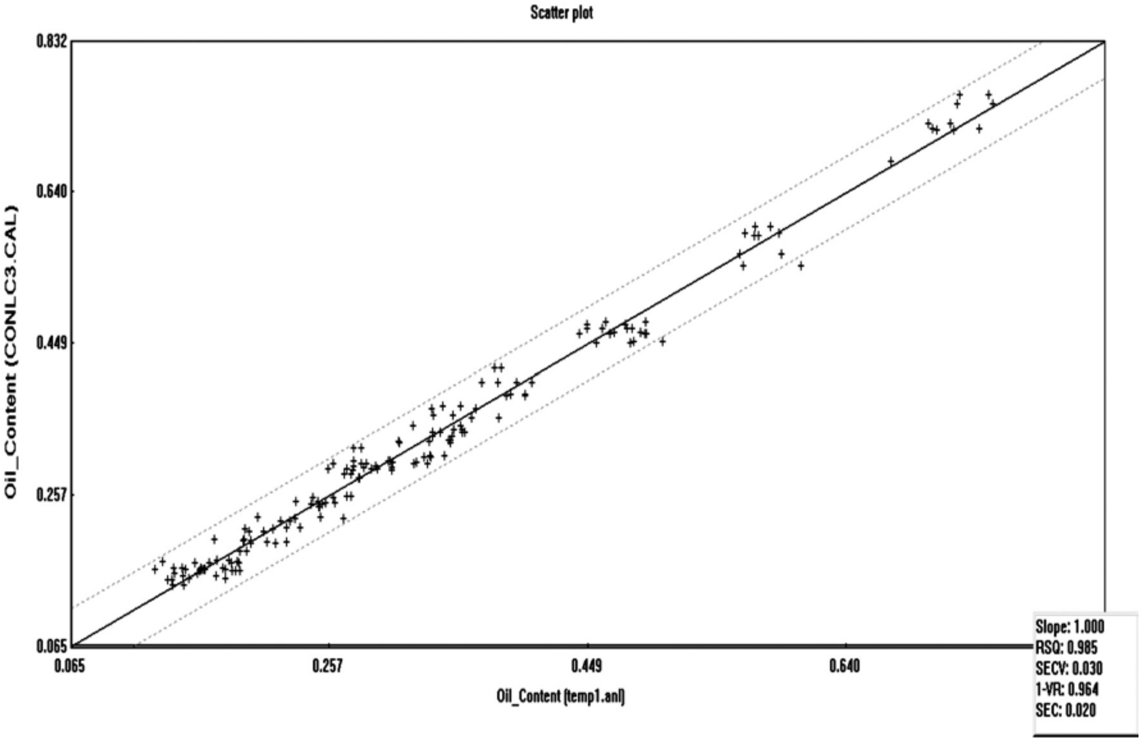

Figure 7. Near infrared (NIR) calibration curves for oil content in steriliser condensate.

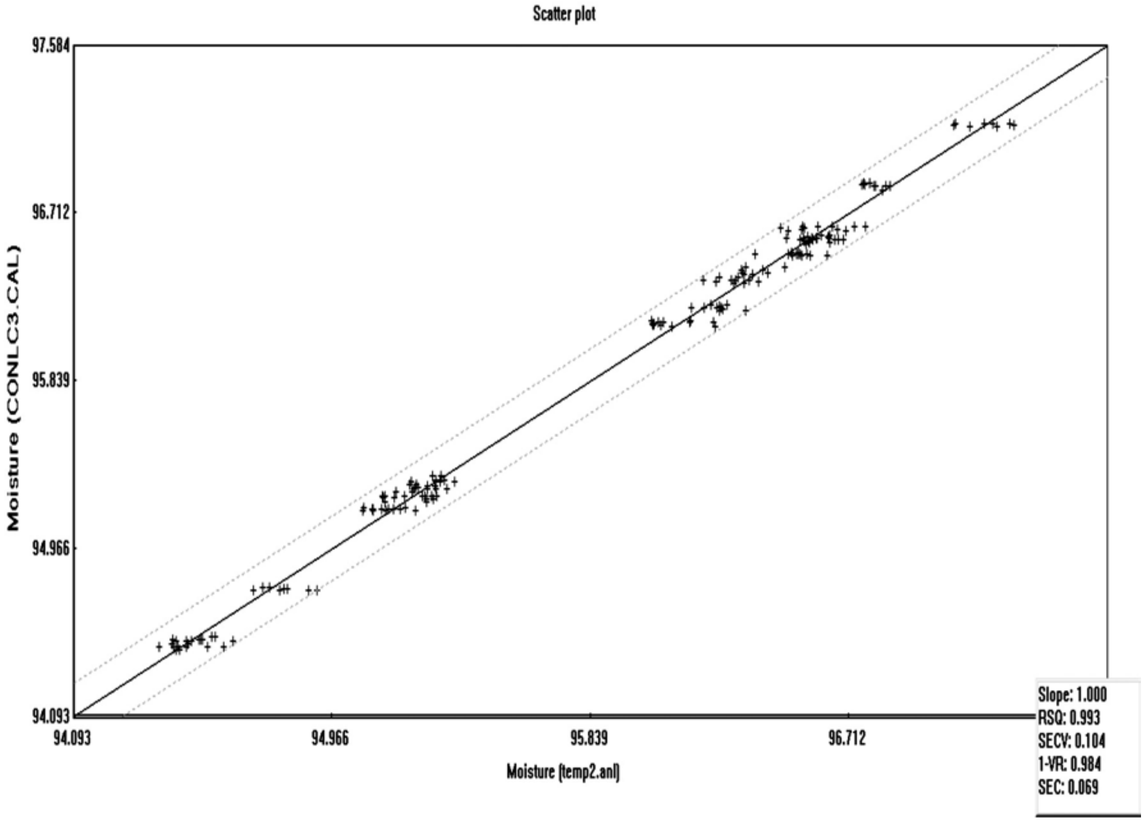

Figure 8. Near infrared (NIR) calibration curves for moisture in steriliser condensate.

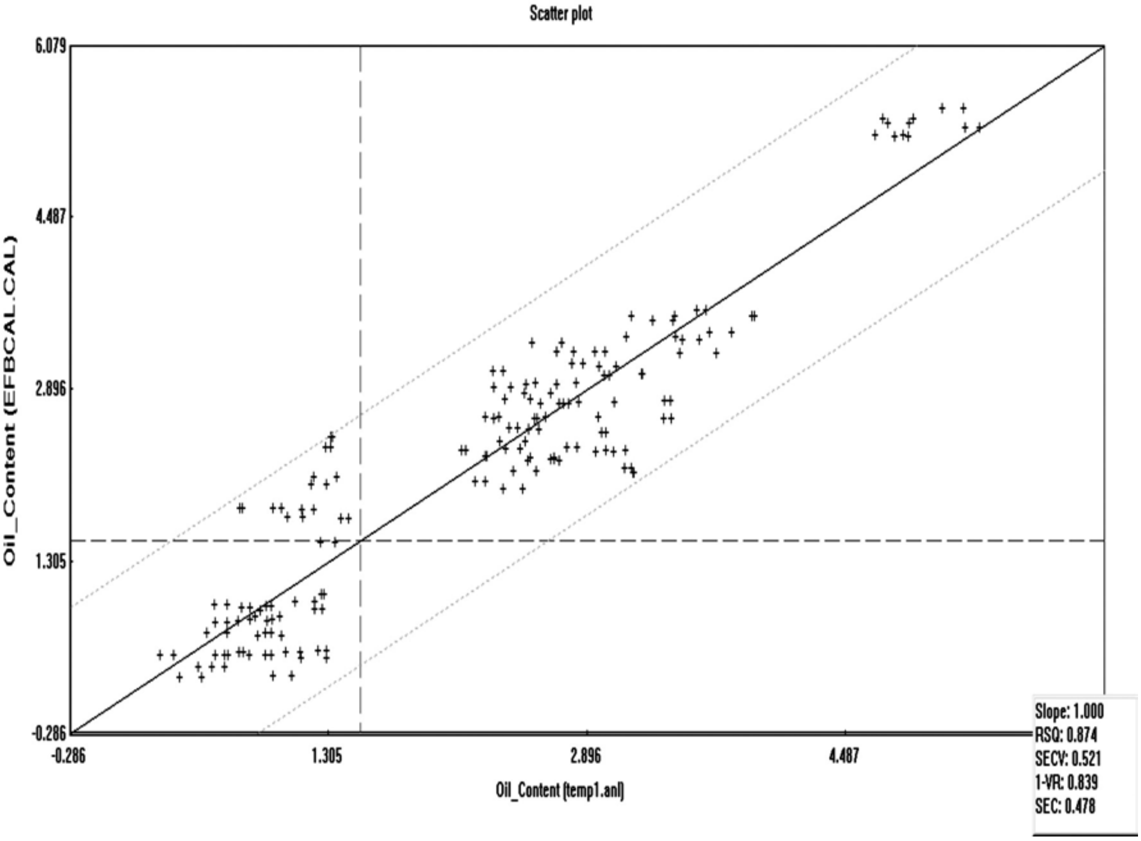

Figure 9. Near infrared (NIR) calibration curves for oil content in empty fruit bunches.

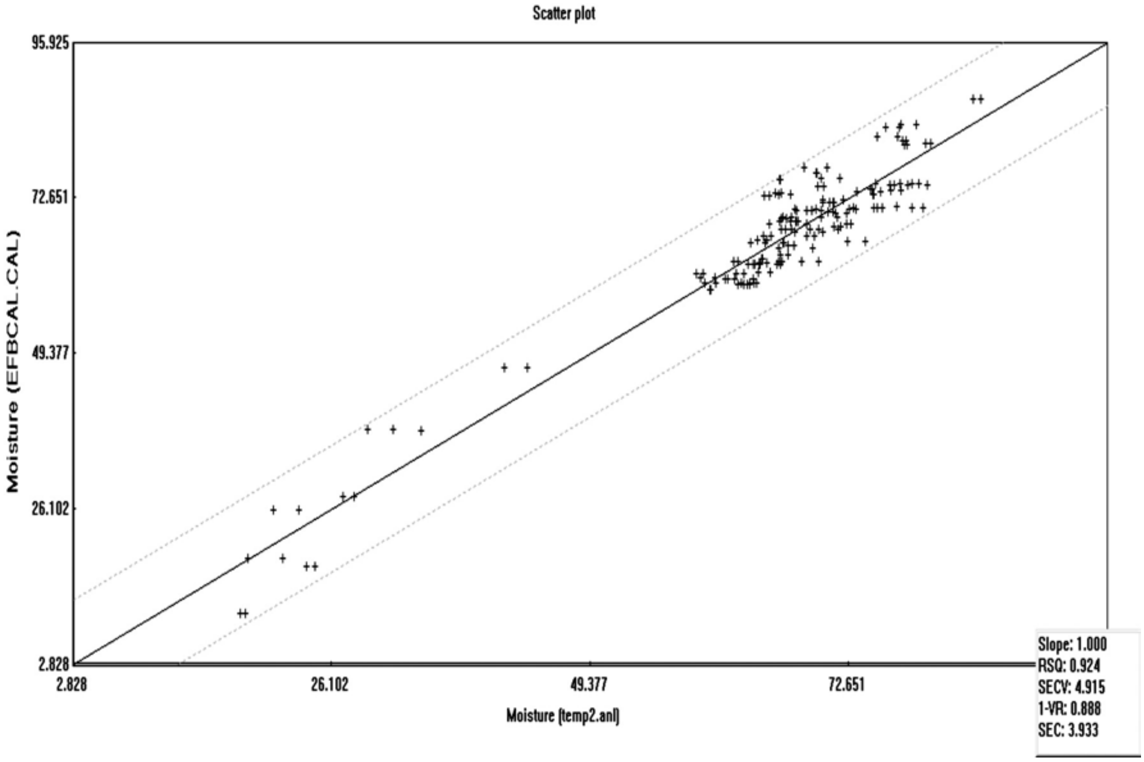

Figure 10. Near infrared (NIR) calibration curves for moisture in empty fruit bunches.

overlapping, interfering absorption bands due to other components or changes in the light scattering intensity.

Complex chemical systems utilise multivariate methods such as PLS extract spectral factors over a broad range of wavelengths that simultaneously relate to the interest constituents concentration and compensate for interfering absorption bands, scattering differences and shifts in band position.

The NIR calibration model will have a SEC that is of the same order of magnitude as the error of the reference method and a correlation coefficient R^2 that approaches 1. The integrity and applicability of the derived calibration model is totally dependent upon the set of data used to create the model. A second independent set of samples could be used to validate the performance of the calibration model to ensure that the derived NIR spectroscopic model is both representative and compensates effectively for encountered interfering absorptions and scattering differences. The adequacy of the calibration method is judged based on the correlation coefficient, R^2, the standard error of prediction (SEP), and the slope and y intercept of the regression line. A robust NIR model usually yield an R and a slope that approaches 1, a y-intercept that approaches 0 and an SEP that is similar to the SEC of the derived NIR calibration model. Respective mathematic formulas are shown in equations (5), (6) and (7).

$$R^2 = \frac{\sum_{i=1}^{N}(y_i^* - \bar{y})^2}{\sum_{i=1}^{N}(y_i - \bar{y})^2} \tag{5}$$

$$\text{SEC} = \sqrt{\frac{\sum_{i=1}^{N}(y_i - y_i^*)^2}{N - K - 1}} \tag{6}$$

$$\text{SEP} = \sqrt{\frac{\sum_{i=1}^{N}(x_i - y_i)^2}{N}} \tag{7}$$

where y_i is the i^{th} value of y for sample, y_i^* is the estimated y_i value given by regression, $\bar{y}$ is mean of y, x is the laboratory reference value determined by a standard test method, N is the number of sample and K is the number of wavelengths used in an equation.

Another statistic term used was coefficient of variation (CV) for the predicted values from cross-validation. CV is a ratio of standard deviation to the mean, multiplied by 100 to express as percentage. CV for NIR predicted values and method reference values were calculated for the validation samples.

Process improvements, raw materials changes over time, malfunction of the analyser or other unknown factors can potentially cause the performance of an NIR method to be compromised. Thus, routine control tests are vital for the process and the analyser monitoring.

Table 2 shows that all the developed calibration curves are having R^2>0.9 and SEP ≈ SEC for all the oil content spectra thus the calibration method is adequate. The spectral that was subjected to SNV, *D* and first-derivative mathematical transformation with a gap of 4 (number of data point over which the derivative is calculated), the factors for data smoothing were 4 and 1 known as 1, 4, 4, 1 mathematical treatment gave the best calibration model for this sets of data.

CONCLUSION

The statistical analysis concluded that all the calibration curves produced from this study are good enough to be transferred to other FOSS InfraXact 7500 NIR spectrometer for palm oil mills laboratory daily operation uses in oil loss monitoring. Probably it is good to add that the accuracy of oil analysis on solids is not as good as that for liquid samples like sludge and steriliser condensate based on the wide band width of the points plotted on the graph.

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REFERENCES

AINIE KUNTOM; SIEW, W L; TAN, Y A; NOR AINI IDRIS; MOHTAR YUSOF; TANG, T S and NUZUL AMRI IBRAHIM (2005). *MPOB Test Methods*. MPOB, Bangi.

BAKSHI, U A and GODSE, A P (2009). *Basic Electronics Engineering*. Technical Publications.

BURNS DONALD, A and CIURCZAK EMIL, W (2008). *Handbook of Near-infrared Analysis*. Third edition. Practical Spectroscopy Series Volume 35. Taylor & Francis Group (CRC Press), USA.

MEHTA, A (2011). *Introduction to the Electromagnetic Spectrum and Spectroscopy*. Pharmaxchange info.

ROMAN M BALABIN; RAVILYA Z SAFIEVA and EKATERINA I LOMAKINA (2007). Comparison of linear and nonlinear calibration models based on near infrared (NIR) spectroscopy data for gasoline properties prediction. *Chemometr Intell Lab., 88(2)*: 183-188.

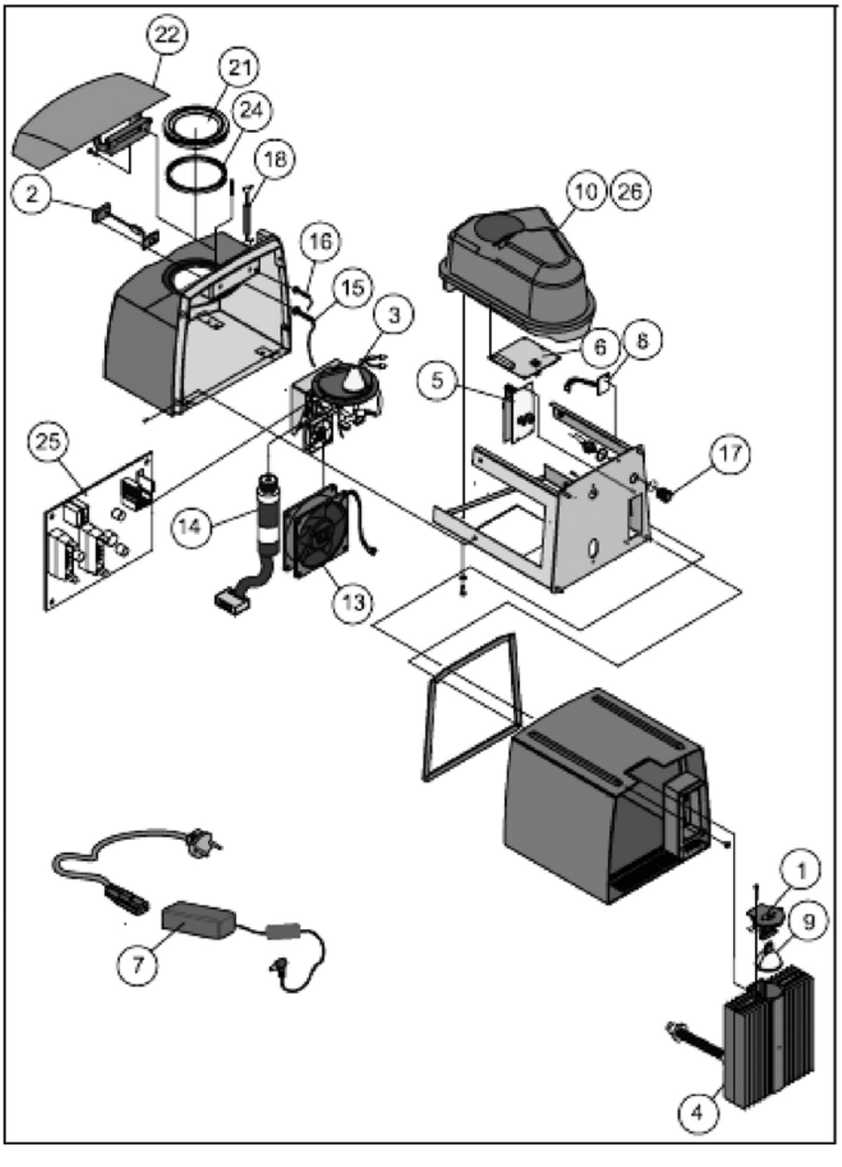
ZULKIFLI ABDUL RAHMAN; ROHAYA HALIM; N RAVI MENON; HASLIYANTI ALIAS; SYED AHMAD MADZLAN SYED IDRIS; MAZLINA SABTU; ROSMAYUDI YUSOF; MOHAMAD ZUBIR YUSOFF; R RAMANI; MOHD HALIM SARBINI; AZHAR MD ZAIN and ZULKHAIR (2010). *Protocol for Measuring Oil Losses.* MPOB, Bangi.

NOMENCLATURE

Symbol	Particular	SI Unit
c	Speed of light, ≈ $3X10^8$	ms^{-1}
f	Frequency	Hz
h	Planck's constant ≈ $6.626068x10^{-34}$	Js
k	Force constant	$kg\ s^{-2}$
m	Mass	kg
n	Integer vibration quantum number	-
q	Displacement coordinate	m
u	Wave number	$m^2kg\ s^{-1}$
v	Vibration frequency	Hz
x	Laboratory reference value	-
y	Spectrometer value	-
y^*	Regression estimate value	-
E	Energy	J
G	Energy levels	$m^2kg\ s^{-1}$
K	Number of wavelengths used in an equation	-
N	Number of sample	-
N_a	Number of atoms in a molecule	-
R	Correlation coefficient	-
V	Potential energy	$m^2kg\ s^{-2}$
χ	Anharmonicity constant	-
λ	Wavelength	m
CV	Coefficient of variation	-
SEC	Standard error of calibration	-
SECV	Standard error of cross-validation	-
SEP	Standard error of prediction	-
R^2	Coefficient of determination	-

Appendix 1

FOSS InfraXact™ Lab Spare Parts Manual



Position Number	Description
1	Lamp Holder
2	RFID Sensor including Gasket
3	Sample Presentation Unit
4	Lamp House with Fibre
5	Instrument Supply Board
6	DSP Board including Cable
7	Power Supply
8	Instrument ID Board
9	Lamp
10	Spectrometer including DSP Board
11	InfraXact Service Standard Kit
13	Fan
14	Cup Motor
15	Cup Position Sensor
16	Lid Position Sensor
17	Power Switch
18	Pneumatic Damper
19	Service Kit Cables
20	Service Kit Gaskets
21	InfraXact Instrument Glass Repair Kit
22	Lid Complete
23	InfraXact Aperture Kit
24	SPU Bearing
25	SPU PCB
26	Exchange Spectrometer including DSP Board