

# Rapid Method for Determining Moisture Content in Crude Palm Oil by Fourier Transform Infrared Spectroscopy

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**ABSTRACT:** A simple, rapid, and direct Fourier transform infrared (FTIR) spectroscopic method was developed for the determination of moisture content of crude palm oil (CPO). The calibration set was prepared by adding double-distilled water to dried CPO in ratios (w/w) between 0 and 13% moisture. A partial least squares (PLS) regression technique was employed to construct a calibration model followed by cross-validation step. The accuracy of this method was comparable to the accuracy of the American Oil Chemists' Society's vacuum oven method, which is used for determination of moisture and volatile matter, with mean difference ( $MD_d$ ) of 0.0105, a coefficient of determination ( $R^2$ ) and a standard error of calibration (SEC) of 0.9781 and 0.91, respectively. It is also comparable to the accuracy of the International Union of Pure and Applied Chemistry's distillation method with  $MD_d$ ,  $R^2$ , and SEC of 0.0695, 0.9701, and 0.65, respectively. The study showed that midband FTIR spectroscopy combined with the PLS regression calibration technique is rapid and accurate for determination of moisture content of CPO samples with a total analysis time of less than 2 min and less than 2 mL of sample.

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**KEY WORDS:** Crude palm oil, FTIR spectroscopy, moisture content, PLS.

Oils and fats and their products are rarely delivered completely dry to customers. The solubility of water in common fats and oils is as high as 0.05–0.30% without physical evidence of its presence (1). In view of the enormous volume of fat and oil and their products traded and exchanged internationally, rapid determination of various quality parameters such as moisture content assumes considerable importance. Although fats and oils and their products are traded on a dry basis and they are generally packaged under optimal conditions, it is virtually impossible to keep liquid, semisolid, or solid materials absolutely anhydrous despite their hydrophobic nature.

The moisture method and moisture and volatile matter method have been developed to provide accurate moisture assays in minimal test time. The American Oil Chemists' Society (AOCS) official methods (2) such as hot-plate (Ca 2b-38), air oven (Ca 2c-25), vacuum oven (Ca 2d-25), and others involve the evaporation of water by heating with or without use

of vacuum for the quickest drying without damaging solids by decomposition, charring, or loss of weight as the result of pyrolysis of portions of the oil. Distillation method 2.602 of the International Union of Pure and Applied Chemistry (IUPAC) (3), official method Ca 2a-45 of the AOCS (2), and AACC method 44-51 of the American Association of Cereal Chemists (4) are entrainment methods used for determination of water in fats and oils and their products. But they are less accurate for values of less than 0.05% moisture. Most of the foregoing methods are rather time consuming and/or have been found to give varying results. In the modified hot-plate method of the AOCS Ca 2f-93 (5), the addition of acetone serves to avoid splattering of the fat or oil during evaporation of the moisture. The Karl Fischer method (3) eliminates the need for heat and is rapid and convenient when compared with older methods; however, it is environmentally hazardous because it uses chemicals such as iodine, sulfur dioxide, pyridine, chloroform, and anhydrous methanol. Fourier transform infrared (FTIR) spectroscopy had been used to determine fat and/or moisture in high-fat products using 1-propanol as solvent (6). In the present study, the FTIR spectroscopic method is developed as a rapid, simple and cost-effective alternative to conventional methods for determining moisture content of crude palm oil (CPO).

## MATERIALS AND METHODS

*Sample and sample preparation.* CPO was purchased from a local refinery. The CPO sample was dried in a vacuum oven for  $3 \pm 1$  h. The drying was carried out at 75°C with internal oven pressure of 100 mm Hg under nitrogen blanketing for 1 h. Heating was repeated several times with addition of nitrogen gas on top of the oil prior to each heating, until a constant weight was achieved after cooling to room temperature in a desiccator containing activated silicates.

Twenty-two calibration samples in duplicate were derived by spiking double-distilled water in certain ratios (w/w) covering the range 0 to 13% moisture. Samples were covered and shaken vigorously using Autovortex mixture SA1 (Stuart Scientific, Redhill, Surrey, United Kingdom) to ensure homogeneity of samples.

*Analysis. (i) AOCS vacuum oven method.* The calibration samples were analyzed in duplicate for determination of

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moisture content and volatile matter using AOCS method Ca 2d-25 (2) in Eyela Vacuum Oven VOS 450SD (Rikakikai Co., Ltd., Tokyo, Japan).

(ii) *IUPAC distillation method.* The same samples were also analyzed in duplicate for moisture content using the IUPAC distillation method 2.602 (entrainment method) for determination of water (3).

(iii) *FTIR spectroscopy scanning.* Each sample was shaken vigorously using an Autovortex Mixer SAI (Stuart Scientific) and a few drops were sandwiched between clean and dry sodium chloride (NaCl) windows. A polytetrafluoroethylene spacer was placed between the windows to give a fixed path-length of 0.1 mm. Cells were fitted in the sample holder in the FTIR spectrophotometer and scanning was carried out for each sample. NaCl windows were rinsed at least three times with pure acetone then dried. The windows used in this study should be made of water-insoluble material. But the use of a low range of moisture content values affects neither the detection nor the NaCl windows.

Samples were scanned using a PerkinElmer 1650 series FTIR spectrophotometer, (Norwalk, CT) with a deuterated triglycine sulfate detector connected to a PerkinElmer model 7300 professional computer. Infrared data system (IRDM) software was used during FTIR data collection.

FTIR data were collected from 64 scans at resolution of  $8\text{ cm}^{-1}$  and strong apodization through the region  $4000\text{ to }600\text{ cm}^{-1}$ . All spectra were ratioed against the background air spectrum, and they were recorded as absorbance values at each data point.

The software program Nicolet Turbo Quant IR—Calibration and Prediction Package version 1.1 (Nicolet Instrument Co., Madison, WI) was used to construct a model from all of the samples used for calibration development. A partial least square (PLS) approach was developed for mathematical treatments of FTIR data (7).

The adequacy of FTIR calibration was assessed on the goodness of fit between distillation method data and FTIR prediction of moisture content values of the 22 samples used during the calibration process. The same comparison of fitness was done between vacuum-oven method data and FTIR prediction of moisture content values for the same samples. In both cases, the assessment of accuracy for PLS equation was based on the standard error (SE) and the coefficient of determination ( $R^2$ ) (8).

*Validation.* The “leave-one-out” cross-validation technique was used for the two tests calibration models, and the accuracy of each equation was assessed according to the standard error of prediction (SEP) and coefficient of determination ( $R^2$ ). The validation step was further investigated by using the mean difference (MD) and standard deviation of the difference (SDD) for repeatability and accuracy between the predicted FTIR data against moisture content values of AOCS vacuum oven method and the IUPAC distillation method.

## RESULTS AND DISCUSSION

*Moisture content measured by AOCS vacuum oven and IUPAC distillation methods.* The range of duplicate moisture

contents of the CPO data set was from 0 to 13% for calibration and cross-validation. The means and standard deviation (SD) for moisture content values of calibration and cross-validation data set were 5.755, 1.926 and 5.63, 1.425, respectively, for the AOCS method and 5.678, 1.729 and 5.677, 1.298, respectively, for IUPAC method as shown in Table 1.

*Absorption bands of water.* The identification of water can easily be confirmed by a study of the O-H, hydrogen (H)-bonded stretching vibration that has a highly characteristic absorption in the frequency region of  $3150\text{--}3500\text{ cm}^{-1}$  as reported by van de Voort *et al.* (9). The absorption near  $3400\text{ cm}^{-1}$ , in the spectrum of the sample mounted on KBr windows, was assigned to water (10). Solomon and Carangelo (11) were able to establish a correlation between band intensity and OH content in coal, but a better correlation was obtained using optical density at  $3200\text{ cm}^{-1}$ . Osawa and Shih (12) measured the absorption intensity of the OH group in coal at  $3400\text{ cm}^{-1}$ .

Water in fatty foods has an HO-H vibration at a frequency of  $1650\text{ cm}^{-1}$  as determined by van de Voort *et al.* (6) and reported by Safar *et al.* (13). Moisture content of a set of standards containing 0.2–2% water in anhydrous MeOH has been measured (14) by relating their moisture content to the height of the water absorption peak at  $1650\text{ cm}^{-1}$  in their FTIR spectra. All  $1650\text{--}1670\text{ cm}^{-1}$  intensity measurements made on spectra of nondried KBr pellets showed some risk of interference from OH bending modes of water in the KBr (15). Bell (16), Luinge *et al.* (17), and van de Voort *et al.* (9) had shown the spectra of water. The mean spectrum of CPO spiked by water shown in Figure 1 indicates that the OH stretching absorption of H-bonding hydroxyl groups occurs in the region  $3074\text{--}3700\text{ cm}^{-1}$ , but not for varying amounts of OH-containing compounds such as monoglycerides, free fatty acids, and hydroperoxides as in oxidized oils (18–21). The region  $1500\text{--}1700\text{ cm}^{-1}$ , as in the correlation spectrum (Fig. 2), showed a correlation band for water, but it was less intense than in the region  $3074\text{--}3700\text{ cm}^{-1}$ , which was selected for this study. Nakanishi and Solomon (22) reported a weak band at  $1640\text{--}1615\text{ cm}^{-1}$  (H–OH bending vibration).

The correlation spectrum presented in Figure 2 shows the spectral regions that had the highest correlation between changes in moisture content information and spectral response as described by Fuller *et al.* (23). For the region  $3074\text{--}3700\text{ cm}^{-1}$ , it appears that there is a good correlation between absorbance and moisture content as obtained from the two classical methods, AOCS and IUPAC. A variance

**TABLE 1**  
Calibration and Cross-Validation Statistics for Moisture Content Values Measured by AOCS and IUPAC Methods<sup>a</sup>

Data set	AOCS method		IUPAC method	
	Mean	SD	Mean	SD
Calibration	5.755	1.926	5.678	1.729
Validation	5.630	1.425	5.677	1.298

<sup>a</sup>AOCS, American Oil Chemists' Society; IUPAC, International Union for Pure and Applied Chemistry; SD, standard deviation.

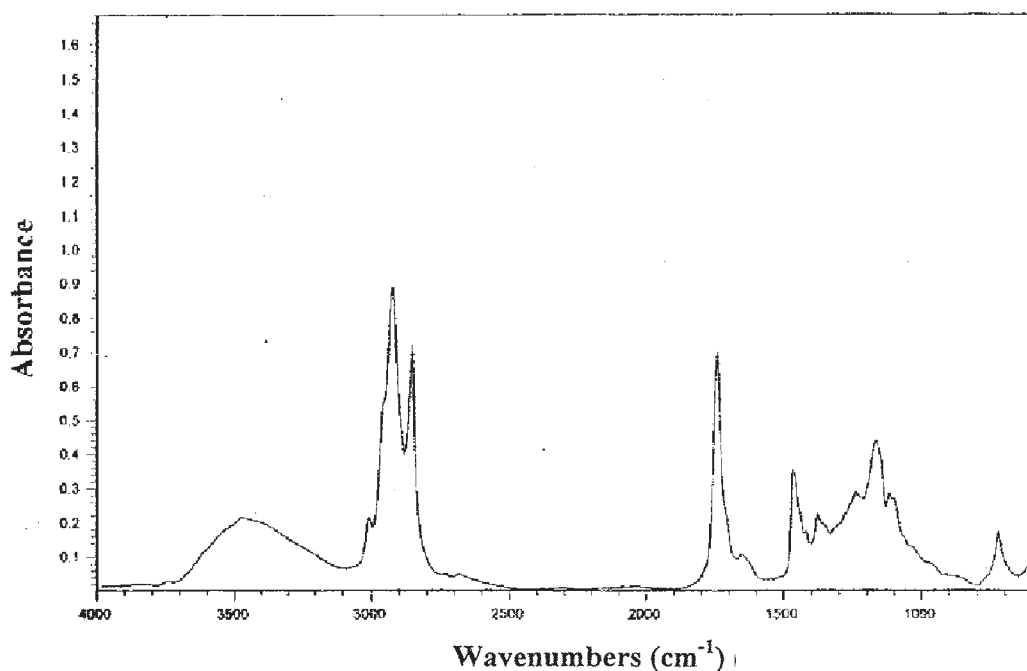


FIG. 1. Mean spectrum of calibration set.

spectrum obtained from the calibration set is shown in Figure 3. Absorption changes at 3074–3700  $\text{cm}^{-1}$  with changes in moisture content values are shown in Figure 4.

From this study, we postulate that the region 3074–3700  $\text{cm}^{-1}$  can be used to develop a calibration model for prediction of moisture content of CPO samples. Table 2 presents the results obtained from the PLS calibration in terms of  $R^2$  and

SEC used to choose the spectral region 3074–3700  $\text{cm}^{-1}$  for determining moisture content for CPO samples.

An FTIR calibration region and PLS regression for the prediction of moisture content for the CPO samples. In using the calibration data set, the SEC for the model was 0.91, and the coefficient of the determination ( $R^2$ ) was 0.9781. A good linear re-

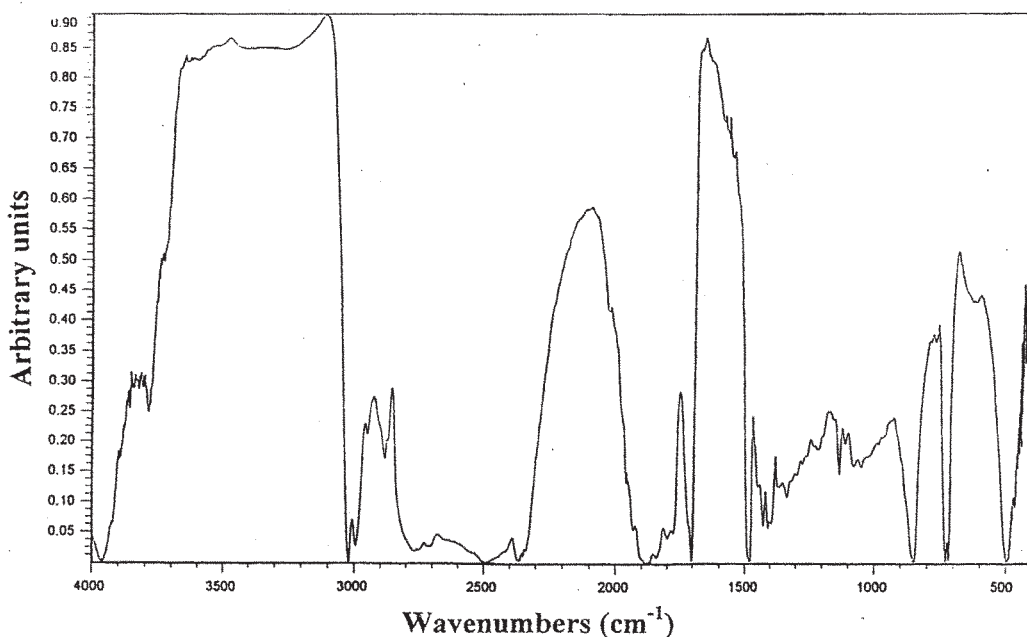


FIG. 2. Correlation spectrum, showing better correlation of water absorption at 3074–3700  $\text{cm}^{-1}$  than 1500–1700  $\text{cm}^{-1}$ .

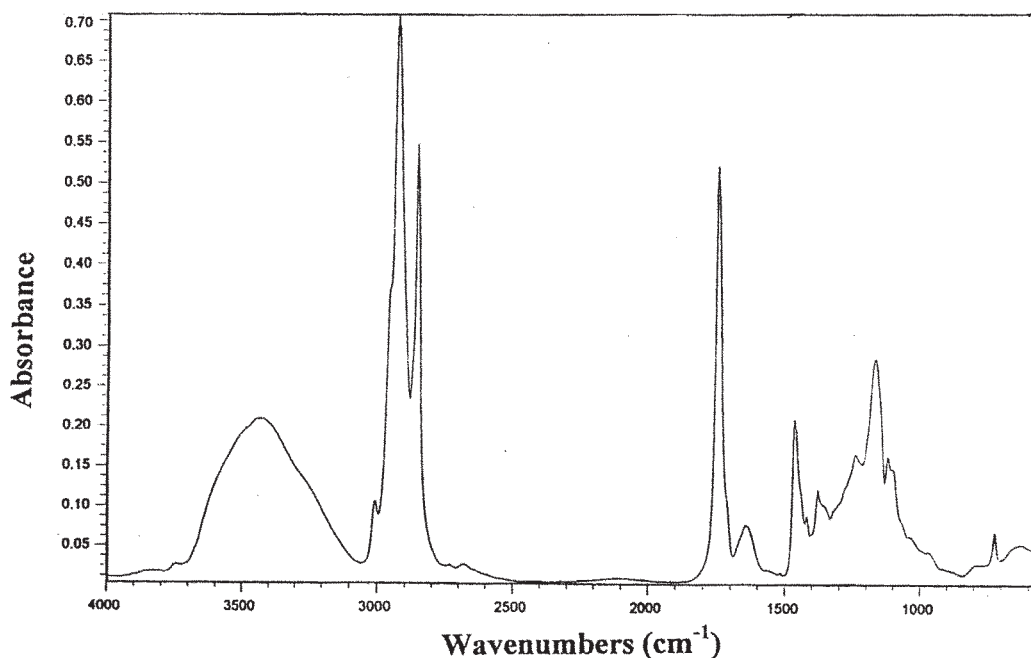


FIG. 3. Variance spectrum obtained from the calibration set., determined by calculating the average absorbance at each wave number position over the entire calibration data set and then calculating the square root of variance about that mean for the entire data set generated the variance spectrum.

gression with the AOCS vacuum oven method-determined moisture content values against FTIR spectroscopic predicted values was obtained ( $y = 0.9681x + 0.0168$ ) that gave an intercept and slope not significantly different ( $P > 0.05$ ) from 0.0 and 1.0, respectively (Fig. 5).

A better calibration model was obtained using the IUPAC

distillation method and the FTIR spectroscopic predicted values within the same wavenumber range ( $3074\text{--}3700\text{ cm}^{-1}$ ) using PLS regression for prediction of moisture content for the same CPO samples. The SEC for this model was 0.651 and  $R^2$  was 0.9701. A linear regression of moisture content values against FTIR predicted values ( $y = 0.9701x + 0.1696$ )

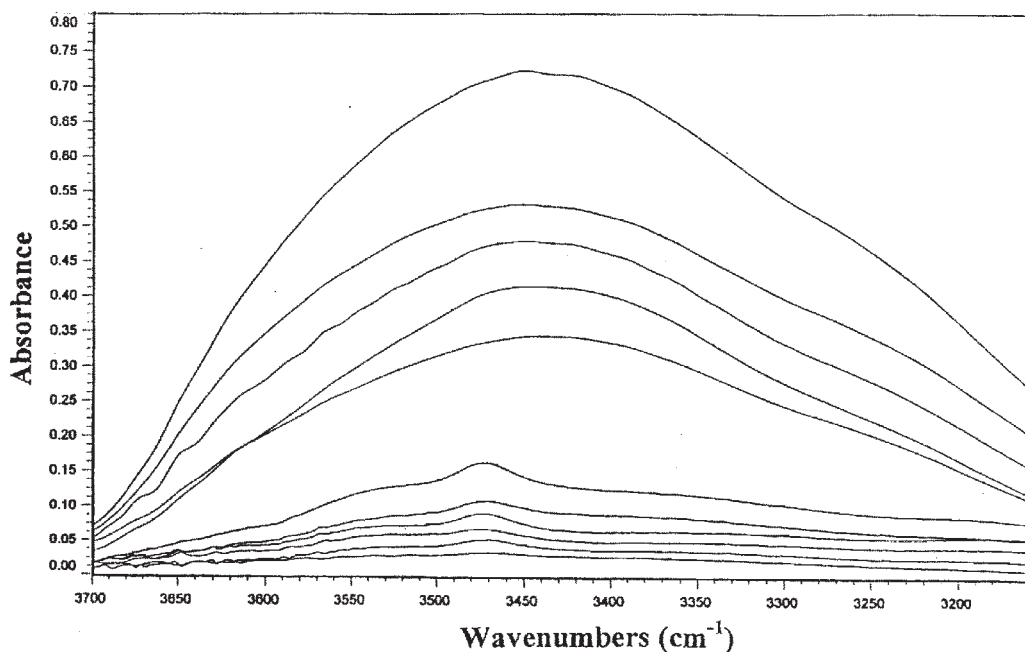


FIG. 4. Absorption changes at  $3074\text{--}3700\text{ cm}^{-1}$  with the changes in moisture content.

**TABLE 2**  
Result of the Developed Calibration Models of AOCS and IUPAC Methods at the Wavenumber Region (3074–3700  $\text{cm}^{-1}$ ) for Moisture Content of CPO Samples<sup>a</sup>

Method	Calibration		Validation	
	$R^2$	SEC	$R^2$	SEP
AOCS	0.9781	0.9147	0.9586	1.4671
IUPAC	0.9701	0.6510	0.9598	0.8635

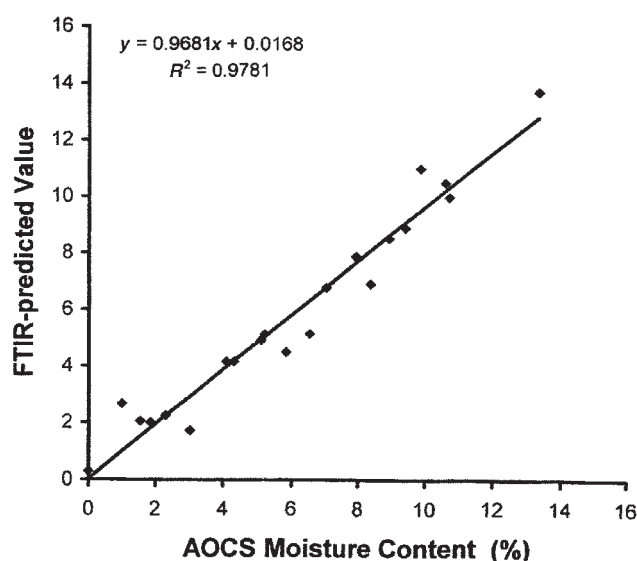
<sup>a</sup> $R^2$ , coefficient of determination; SEC, standard error of calibration; SEP, standard error of prediction for validation; CPO, crude palm oil; for other abbreviations see Table 1.

also gave an intercept and slope that were not significantly different ( $P > 0.05$ ) from 0.0 and 1.0, respectively (Fig. 6).

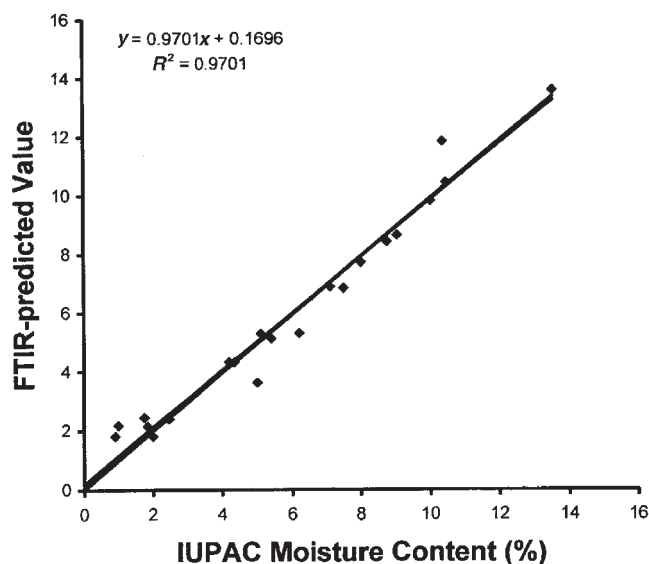
Expressing the average of the products of deviations for each data point pair in two data sets generating the coefficient of variation (CV) is a method for describing the accuracy of the FTIR calibration. Clark *et al.* (24) decided that CV less than 20% are acceptable for most analytical purposes. The CV of both equations (see Figs. 5 and 6) to predict moisture content in CPO in this study was about 12–13%.

The “leave-one-out” cross-validation technique was carried out to provide an estimate of the overall accuracy of predictions. The intercept and slope of the linear regression line are shown in Figure 7. A plot of classical IUPAC distillation method determination vs. FTIR-predicted moisture content value for the cross-validation ( $y = 0.9534x + 0.1498$ ) was not significantly different ( $P > 0.05$ ) from 0.0 and 1.0, respectively, with SEP of 0.863, and  $R^2$  of 0.9598, as shown in Table 2. The mean difference  $MD_a$  and standard deviation of difference  $SDD_a$  were 0.0695 and 0.0169, respectively (Table 3).

When the “leave-one-out” cross-validation technique was carried out for the set predicted with the calibration model in the case of the AOCS vacuum oven method, the SEP was



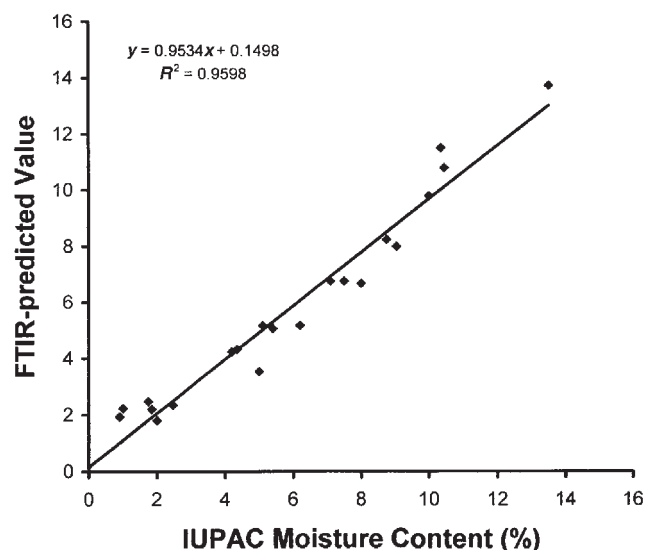
**FIG. 5.** American Oil Chemists' Society (AOCS) vacuum oven method compared with Fourier transform infrared (FTIR) spectroscopic predicted values, calculated with partial least squares (PLS) calibration.



**FIG. 6.** International Union of Pure and Applied Chemistry (IUPAC) distillation method compared with FTIR spectroscopic predicted values, calculated with PLS calibration. For abbreviations see Figure 5.

1.467,  $R^2$  was 0.9586,  $MD_a$  was 0.0105 and  $SDD_a$  was 0.0475. The intercept ( $-0.1936$ ) and slope (1.0082) for the linear regression line were not significantly different ( $P > 0.05$ ) from 0.0 and 1.0, respectively (Fig. 8).

Table 3 compares the obtained data in terms of MD, SDD for accuracy (a) and repeatability (r) between duplicates for each of the two classical methods, and FTIR-predicted results. The two classical methods and FTIR have comparable  $MD_r$  and  $SDD_r$ . The result in terms of  $MD_a$  and  $SDD_a$  indicated that moisture content of CPO could be measured with good accuracy by FTIR spectroscopy. A general comparison of the three methods (Table 4) shows the FTIR method is

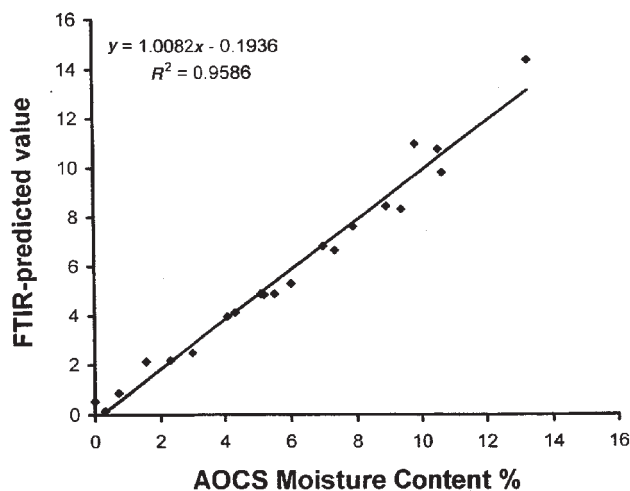


**FIG. 7.** IUPAC distillation method vs. FTIR-predicted moisture content for the cross-validation. For abbreviations see Figures 5 and 6.

**TABLE 3**  
Calibration Statistics for Moisture Content Values Obtained by Classical Methods and the FTIR Method<sup>a</sup>

Statistics	AOCS method	IUPAC method	FTIR method
MD <sub>r</sub>	0.1077	0.0463	0.0216
SDD <sub>r</sub>	0.0391	0.0680	-0.0520
Minimum value	0.00	0.00	-0.302 and -0.207
Maximum value	13.25	13.50	13.60 and 13.73
MD <sub>a</sub>	0.0105	0.0695	—
SDD <sub>a</sub>	0.0475	0.0169	—

<sup>a</sup>FTIR, Fourier transform infrared spectroscopy; MD, mean difference; SDD, standard deviation of difference; r, repeatability; a, accuracy; for other abbreviations see Table 1.



**FIG. 8.** AOCS vacuum oven method vs. FTIR-predicted moisture content for the cross-validation. For abbreviations see Figure 5.

rapid, sensitive, uses small amounts of sample and no toxic chemicals compared to the classical methods.

From this study, we conclude that an FTIR spectrometer equipped with a transmission cell, can be used to develop equations for determining moisture content of CPO. The prediction of moisture content depends on measuring absorbance of a single band, such as the OH stretching band at 3074–3700  $\text{cm}^{-1}$ . The complete FTIR analysis to determine moisture content in CPO can be performed in less than 2 min per sample. A rapid moisture content determination by FTIR spectroscopy is therefore suitable for practical on-line quality control laboratories. Further advantage of FTIR method is that it is environmentally friendly, as no added chemicals are needed for the analysis.

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**TABLE 4**  
A General Comparison Between the Three Methods Used in the Study<sup>a</sup>

	AOCS method	IUPAC method	FTIR method
Amount of sample	5–10 g	20–100 g	1–2 g
Chemicals	—	100–300 mL xylene/toluene	—
Time	>3 h	>30 min	2 min
Limits of detection	0.05%	1% or more	<0.05%

<sup>a</sup>For abbreviations see Tables 1 and 3.

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