FOURIER TRANSFORM NEAR - INFRARED SPECTROSCOPY FOR NONDESTRUCTIVE AND RAPID MEASUREMENT OF MOISTURE CONTENT OF PADDY

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Abstract: The accurate measurement of moisture content of paddy is essential for the effective supervision of its quality. The feasibility of measuring moisture content in paddy was investigated by Fourier Transform Near-Infrared (FT-NIR) spectroscopic technique. A calibration model was developed using paddy standards of varying moisture content in the near-infrared region (4000–12000 cm^{-1}). The developed model was validated. FT-NIR spectroscopy with chemometrics, using the PLS–first derivative plus vector normalization method could predict the moisture content in paddy samples accurately up to an correlation coefficient (R^2) value greater than 0.97, RPD (residual predictive deviation) greater than 6 and root mean square error of cross validation (RMSECV) value less than 0.5 with 5 factors in the prediction model. The developed model was applied to predict moisture content in paddy samples within 10-12 seconds. The developed procedure was further validated by recovery studies by comparing with oven method and indirect method (digital moisture meter) of moisture determination.

Key words: NIR Spectroscopy, chemometrics, paddy, moisture content, calibration, validation, PLS factor

INTRODUCTION

Paddy is one of the most important crops grown in India. In storage conditions contrary with the prescribed moisture content occurs deterioration of paddy. Moisture

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content is the key parameter in paddy it plays a major role in the shelf life and storage time. Indeed, it has been shown that the decrease in the moisture content induces an increase in the shelf-life and a decrease in the spoilage occurrence. When the moisture content increases, water from the process of respiration accumulates and supports further metabolic processes. Generated heat contributes to even more intense respiration and may eventually damage sensory and physiological properties of grain or spontaneous combustion may occur [1].

There are two major methods to determine the moisture content of grains: direct methods and indirect methods. Direct methods, the water content in the kernels are removed totally. However, direct method is tedious, destructive, relatively expensive and time-consuming, as well as they require highly skilled operators [2]. Indirect methods in which electrical conductance and capacitance characteristic of the grain is measured that are affected by moisture content of the grain. These techniques are rapid and easy to use. However, they must be calibrated by standard moisture content that is measured by a direct method. Even though indirect method consume less time as compared to direct method it is less accurate. Rice milling industries, Food Corporation of India, Central Warehousing Corporation and various paddy research stations are suffer during measurement of moisture content in paddy due to time consuming, destructive and less accurate methods.

Near infrared spectroscopy (FT-NIR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, which is light with a longer wavelength and lower frequency than visible light. In recent years, NIR spectroscopy has become a valid tool supporting destructive methods. The application of near infrared spectroscopic technique for the quantitative analysis of food products and commodities is nowadays widely accepted. Several studies have been reported on the use of NIR spectroscopy as a rapid and cost-effective analytical tool to determine the food structure and properties in fundamental research and as on-line sensors for monitoring process [3]. The NIR spectrum of an organic material gives a global signature of composition based on the assessment of the organic chemical structures containing O-H, N-H and C-H bonds [4]. Advantages of near infrared spectroscopy include minimal sample preparation (may be performed *in situ* in many instances), rapid analysis and much deeper sample penetration than far or mid infrared radiation [5].

Nevertheless, only few studies have addressed the application of NIR spectroscopy in moisture content studies; [6] used NIR spectroscopy to determine the moisture content in fishmeal and [2] studied the water content of surimi by NIR spectroscopy but none of the researchers determine the composition of paddy by FT-NIR spectroscopy. The aim of this work was to evaluate the feasibility of FT-NIR spectroscopy as a rapid non-destructive approach for moisture content measurement of paddy.

MATERIAL AND METHODS

Raw Material

Paddy was obtained from centre farm, located in Tamil Nadu Agricultural University, Coimbatore of Tamil Nadu, India and used for the study. The paddy was

cleaned manually to remove all foreign materials such as dust, dirt, chaff and immature paddy.

Destructive methods of estimation of moisture content in paddy

Direct method / Oven method

As per Association of Official Analytical Chemists [7] standard method, 25-30 g of whole paddy was dried at 130℃ for 14-16 h.

Indirect method / Digital moisture meter

Indirect method of moisture measurement was done by using PSAW digital moisture meter. The operation of PSAW digital moisture meter is based on the fact that the electrical conductivity of a moist material is directly proportional to the amount of moisture contained in it. Electrical conductivity also varies with the temperature. A built in temperature sensor along with microprocessor circuitry of the instrument compensate for these variations. The paddy sample of the entire lot thoroughly mixed before testing. A measuring cup of C volume was filled with the paddy up to its brim. The measuring cup was properly shaken and leveled to avoid superfluous empty spaces in between the grain. The paddy material was transferred into the test cup. Than the test cup containing the sample in its housing in such a manner that the guide stems of the cup snuggly fits into the hole in the body base. Then selected compression thickness required for paddy (3.25) was selected by rotating the smaller handle in anticlockwise direction. After that the ratchet handle fitted into the open end of bevel pinion and compressed the sample until the reading on the main scale and the circular scale divisions together give the correct thickness reading. Push type switch on the moisture meter was pressed to take the reading after a count down from 10 to 1. The moisture content display had been gave the direct moisture percentage after count down.

Moisture Content Adjustment

The initial moisture content of paddy was determined using the hot air oven (at 130±2˚C until a constant weight was reached) and digital moisture meter. The initial moisture content of paddy was found to be 14.34 % (wb). In order to achieve the desired moisture levels for the study, paddy samples were conditioned by adding calculated quantity of water. The samples were kept in a refrigerator at 4±1°C for a minimum period of 7 days for the moisture to distribute uniformly throughout the paddy. The moisture contents of the samples were equilibrated as per the procedures of [7]. The required amount of sample was withdrawn from the refrigerator and reconditioned at room temperature (30±2°C) before conducting each test [8].

FT-NIR spectroscopy

FT-NIR spectra were recorded on multipurpose analyzer (MPA) (Bruker Optics, Germany) equipped with an integrated Michelson interferometer; highly sensitive PbS 12000-4000 cm^{-1} detector, multiple NIR measurement accessories for different sampling techniques combined with opus 7.2 software. For the current study spectra's were collected in diffuse reflectance mode with sphere macro sample integrating sphere

measurement channel. The spectra were acquired in reflectance mode directly on the paddy, over the range 12000–4000 cm^{-1}. For each sampling, 15 g of paddy were analyzed at room temperature and the average spectra were used for further evaluations.

Calibration and Validation Method

The samples were divided into different portions for standard preparations (15 gram each). Moisture content was estimated in 150 samples by using digital moisture meter and air oven method. The standard values were fed into NIR library and 50 samples were validated by using suitable chemometric method.

Data analysis

The OPUS 7.2 software package was used for processing the data and FT-NIR models were developed with the full calibration data set. The spectral data were analyzed using PLS regression with various preprocessing techniques. In this study three spectral preprocessing methods were applied comparatively; it includes vector normalization, first derivative and first derivative plus vector normalization. Vector normalization normalizes a spectrum by first calculating the average intensity value and subsequent subtraction of this value from the spectrum. The sum of the squared intensities is calculated and the spectrum is divided by the square root of this sum. This method is used to account for different samples thickness. The performance of final PLS model was evaluated in terms of root mean square error of cross validation (RMSECV), RPD (residual predictive deviation) and correlation coefficient of determination R^2. Ratio of standard deviation to standard error of prediction gives RPD value (SD/SEP). The accuracy of the calibration models is obtained according to the largest values of R^2 and RPD and smallest values obtained for RMSECV for cross validation.

RESULTS AND DISCUSSION

Spectral information

A calibration models were developed using moisture content standards of varying concentrations in the near-infrared region (4000–12500 cm^{-1}) is shown in Fig. 1. From the figure it is seen that almost spectra of all samples are parallel. Which means the response of the detector for the sample is linear within the range of study and thus may give better results [9]. As the spectra show similar basic FT-NIR spectral patterns, mathematical transformations were required to use the FT-NIR data for quantitative analysis. Despite the lack of distinct peaks, it has been shown the PLS can extract relevant information for quantitative determinations [10].

Fig. 2 shows the FT-NIR spectra of moisture content which has major peaks at absorbance bands (wave numbers) of 3633.42, 3996, 5184, 6834.85 and 8316 cm^{-1}. These true peaks were selected after smoothing the spectrum to avoid interference due to noise. Each chemical bond in a molecule vibrates at a frequency which is characteristic of that bond. A group of atoms in a molecule may have multiple modes of oscillation caused by the stretching and bending motions of the group.
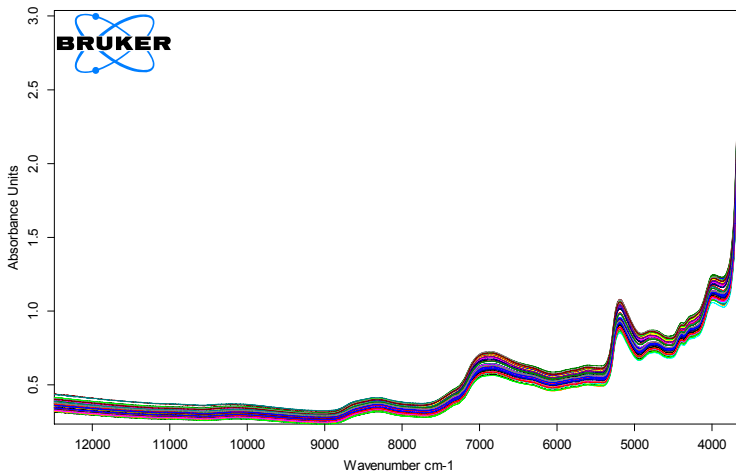
Figure 1. Spectra of paddy samples

The fundamental vibrations in the 4000–3500 cm^{-1} region are generally due to O–H, C–H and N–H stretching. O–H stretching produces a broad band that occurs in the range 3700–3600 cm^{-1}. Hydrogen bonding is very important effect in infrared spectroscopy. This bonding influences the bond stiffness and so alters the frequency of vibration. The presence of hydrogen bonding is of great importance in a range of molecules [11].
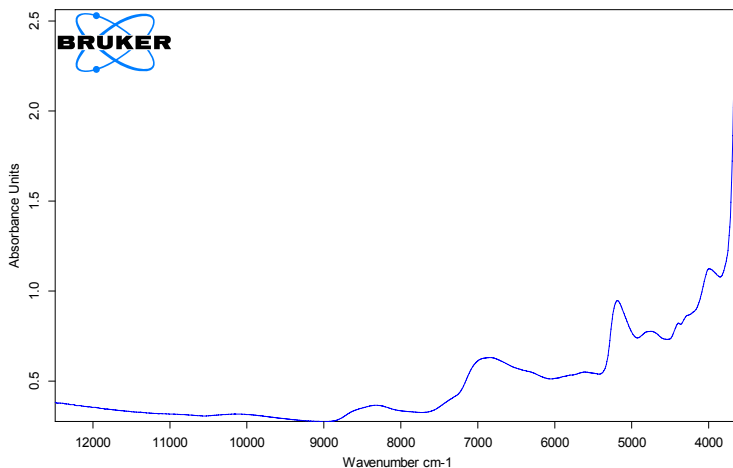

Figure 2. Preprocessed FT- NIR Spectra of paddy sample

Major peaks at absorbance bands or wave numbers of 5184 and 6834.85 cm^{-1} may be due to the OH stretching plus OH bending and first overtone of OH anti-symmetric stretching plus OH symmetric stretching of moisture content respectively. Peaks at 8316 cm^{-1} may be due to second overtone of symmetric stretching (–CH bonds) of methyl (–

CH$_3$) groups. Stretching a bond requires more energy than to bend it. The energy or frequency that characterizes the stretching vibration of a given bond is proportional to the bond dissociation energy. Water molecule has OH groups on structure; hence, the peak may play an important role in the estimation of moisture. Some minor peaks observed in the paddy spectrum may be due to unknown bond vibrations.
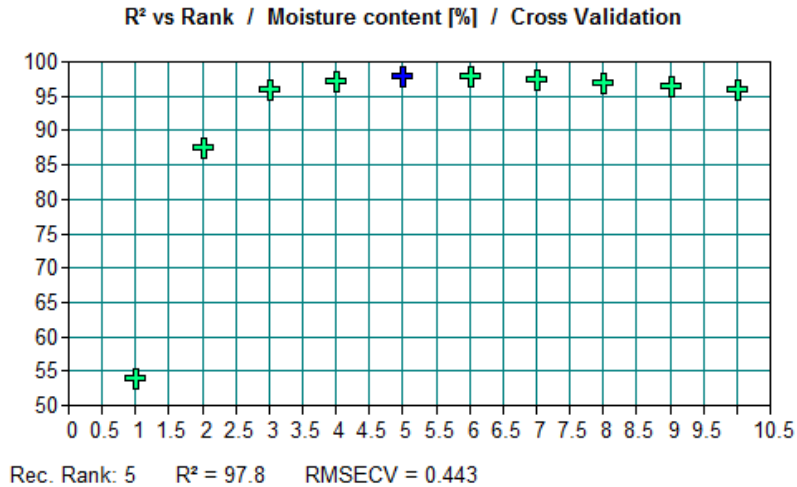

Rec. Rank: 5   R^2 = 97.8   RMSECV = 0.443

Figure 3. R^2 value as a function of PLS factor

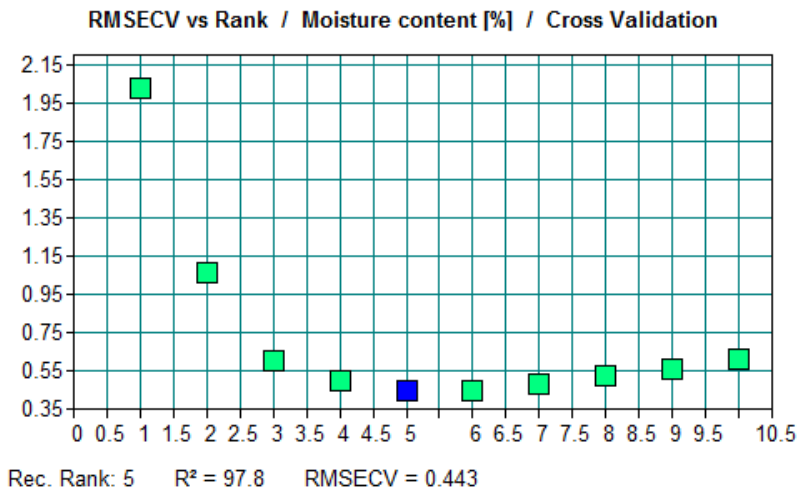Rec. Rank: 5   R^2 = 97.8   RMSECV = 0.443

Figure 4. RMSECV as a function of PLS factor

Figures 3, 4 and 5 show the R^2, RMSECV and RMSEE values plotted as a function of PLS factors for determining moisture content with first derivative plus vector normalization method as the pre-processing technique. First derivative method emphasizes steep edges of a peak. It is used to emphasize pronounced, but small features

over a broad background. Seen from figure, R^2 value increased up to certain limit and reached a maximum value after that it slightly decrease. RMSECV value decreases sharply up to the recording rank of 5 with initial factors and maintain the constant value as PLS factor increases from 5 to 6. RMSEE value decreases sharply if PLS factor increase. From the figure, conform that initial PLS factor had high impact on R^2, RMSECV and RMSEE values. If PLS factor increases it increase the R^2 value and decrease the RMSECV and RMSEE value.
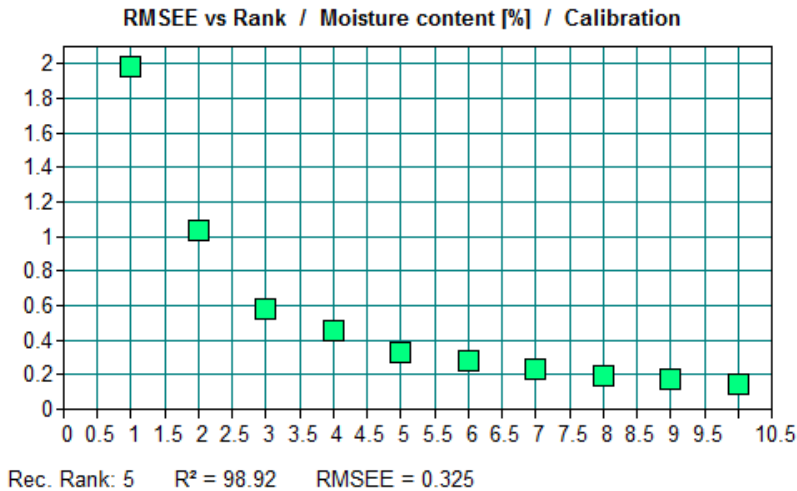

Rec. Rank: 5 R^2 = 98.92   RMSEE = 0.325

Figure 5. RMSEE as a function of PLS factor

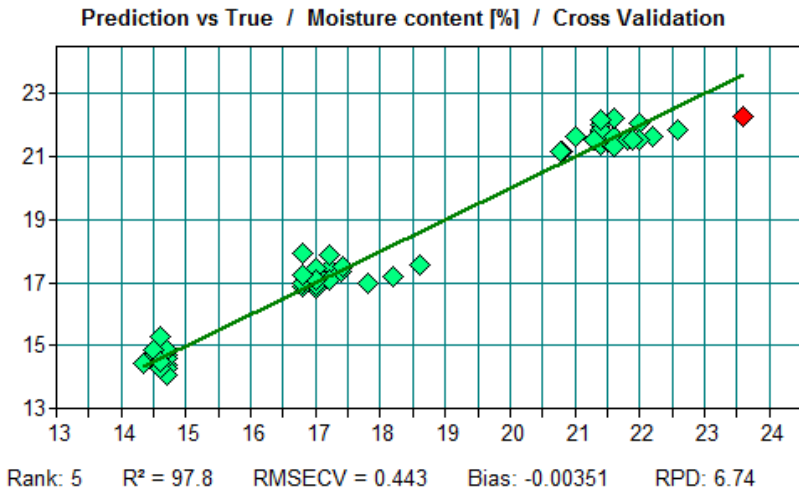Rank: 5 R^2 = 97.8   RMSECV = 0.443   Bias: -0.00351   RPD: 6.74

Figure 6. Cross validation of paddy samples for moisture content

Cross validation was also done to check the calibrated values are shown in Fig. 6. The optimum number of factors is determined by the lowest RMSECV and highest value

for R^2 and RPD. PLS regression method gave R^2 values of 97.8 and RMSECV value of 0.443 respectively. RPD value was more than 6. If RPD value lower than 1.5 is considered insufficient for most applications while NIR cross validation models with values greater than two is considered excellent [12]. The results of this study clearly indicate the efficiency of FT-NIR for this application.

Comparison analysis of paddy samples with conventional methods

Paddy samples prepared were analyzed by FT-NIR spectroscopy and developed chemometric method was applied to quantify the moisture content in paddy samples. Results obtained from FT-NIR spectroscopy were compared with that of the laboratory methods are shown in Table 1. Results obtained from FT-NIR method were found to be approximately equal to air oven and digital moisture meter method.

*Table 1. Comparison of results obtained by air oven, indirect and FT-NIR methods
for moisture content determination*

	Moisture content by hot air oven method (%, w.b.)	*Moisture content by digital moisture meter (%, w.b.)*	*Moisture content by FT-NIR method (%, w.b.)*
Min	*14.34*	*14.52*	*14.07*
Max	*23.6*	*22.47*	*22.28*
Mean	*17.83*	*17.94*	*17.84*
SD*	*3.008*	*3.11*	*2.98*

*Standard deviation

CONCLUSIONS

Results of this study show that NIR spectroscopy could support the conventional techniques in studying the moisture content of paddy. The main advantage of using the NIR spectroscopic techniques is to rapidly draw a profile of the paddy related to its quality. Lower values of RMSECV and RMSEE and relatively higher values of R^2 showed that NIR spectroscopy has potential to predict the moisture content of paddy nondestructively with almost same accuracy as that of laboratory method. The developed models ware applied to forecast moisture content in paddy samples within 15 seconds. This study is useful for CWC (central warehousing corporation) at the time of procurement of paddy from farmers and various paddy research institutions for analyzing the quality of paddy.

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FURIJEOVA TRANSFORMACIJA SPEKTROSKOPIJE U BLISKOJ INFRACRVENOJ OBLASTI ZA NEDESTRUKTIVNO I BRZO MERENJE SADRŽAJA VLAGE U ZRNU PIRINČA

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Sažetak: Tačno merenje sadržaja vlage u celom zrnu pirinča je osnova efikasne kontrole njegovog kvaliteta. Primenjivost merenja vlage u celom zrnu pirinča bilo je ispitivano Furijeovom transformacijom sprektroskopske tehnike u bliskoj infracrvenoj oblasti (FT-NIR). Kalibracioni model je razvijen upotrebom standarda variranja sadržaja vlage za pirinač u bliskoj IC oblasti (4000–12000 cm^{-1}). Razvijeni model je ocenjen. FT-NIR spektroskopija sa hemometrijom, upotrebom PLS–prvih derivata plus metod normalizacije vektora može da predvidi sadržaj vlage u uzorcima pirinča sa tačnošću do

koeficijenta korelacije (R^2) većeg od 0.97, RPD (rezidualna devijacija predviđanja) veća od 6 i greška korena srednjeg kvadrata unakrsne validacije (RMSECV) manja od 0.5 sa 5 faktora u prediktivnom modelu. Razvijeni model bio je primenjen da predvidi sadržaj vlage u uzorcima pirinča za 10-12 sekundi. Razvijeni postupak dalje je ocenjivana povratnim studijama poređenjem sa metodom rerne i indirektnim metodom (digitalni merač vlage) za određivanje vlažnosti.