Dye Rubber Content in Latex Analyzer by Fourier-transformed Transflectance Near Infrared Spectroscopy

Sayun Phansomboon[1*], Sujin Jenweerawat[2],
Vichien Keeratinijakal[2]and Panuwat Supprung[3]

ABSTRACT

The objective of this study was to evaluate the ability of fourier-transformed near infrared spectroscopy (FT-NIR) to determine dye rubber content (DRC) in field latex, samples were measured in the long wavelength region (1000 nm – 2495 nm) the sample range of 20.0% to 40.0% sample temperature was controlled at 25 °C, calibration set n = 90. The samples were scanned in a circular cell cup and reflectance data were stored as logarithm of the reciprocal reflectance (log1/R). The calibration and validation equation were developed from the number of factors used in the calibration and validation equation of F_5. The Multiple correlation coefficients (R) of calibrations of 0.99, validation of 0.98 with standard error of calibration *(SEC)* values of 4.63, bias-corrected standard error of prediction *(SEP)* of 4.68 and the average of difference between actual value and NIR-value *(bias)* values calibration set of 0.12, validation set of 0.98 was

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[1] Program in Tropical Agriculture, Faculty of Agriculture, Kasetsart University, Bangkhen, Bangkok, Thailand

[2] Department of Agronomy, Faculty of Agriculture, Kasetsart University, Bangkhen, Bangkok, Thailand

[3] Department of Postharvest and Agricultural process Engineering, Faculty of Engineering, Rajamangala University of Technology Isan, Khon Kaen Campus, Khon Kaen, Thailand

The best model were generate of original spectra show the FT-NIR spectroscopy for prediction the dye rubber content of fresh latex.

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Keywords: Detection, calcium chloride salts, rubber cublum, Near-Infrared Spectroscopy

Introduction

The fresh latex was essential raw material for para rubber trees (*Hevea brasilisis*), DRC the most requisite issue in community enterprise and concentrate latex industrials. In Thailand, by the current system war the parameter for trading fresh latex, the price paid to vendor depends on dye rubber content. However, the current method analysis is randomly approximated by the convention method hot-air-oven the methods it takes a long time approximately 24 hours to process and the gravimetric method (metrolac) affected by many environmental parameters in was destructive and the latex sample contain high variables regarding the variety, pararubber estate management, maturity, harvesting and etc, based on the total volume of latex produced annually in Thailand will be lost from farmers or trader if the trader over or underestimates the DRC, the para rubber farmers at a possible disadvantage. Therefore, an accurate and dye rubber content measurement system is required to make a fair trading for both traders and farmers. It is non-destructive discrimination monitoring of sample properties was of great importance to ensure the generally accepted that the quality of the field latex and concentrated latex by fourier-transformed near infrared (FT-NIR) Spectroscopic is transmission and reflectance measurements long-wavelength techniques have been used as a latex is regarded as a colloidal dispersion of rubber hydrocarbon in water, the diameter of whose molecular aggregates, range from 0.5 to 1.0 micron (1/1000 th of a mm). In addition to rubber hydrocarbon, latex contains proteinaceous and nitrogenous substances, carbohydrates, lipids, inorganic ions, carotenoids, resins and enzymes. Being a natural product, the proportions of the above substances in latex varies depending on various factors such as clone, season, soil conditions, tapping method and the frequency, the age of the tree, etc. Therefore, the density of latex also varies depending on the composition of latex, the main factor which influences the variation of density in NR latex. and cost-effective analytical way to assess latex quality. A number of studies have reported calibration models for determining the protein content models for DRC analysis.

Near infrared spectroscopy (NIR) has received considerable attention in the last years, as a tool for rapid, non-destructive, nonexpensive (1–5 % of the wet chemistry procedure cost), of simple application and that allows simultaneous assessment of multiple parameters of biomass composition [1,2]. The combination of NIR with chemometric tools allowed the development of multivariate calibration models for the rapid analysis of the chemical composition of feedstocks

To ensure reliable prediction using the correlation of NIR spectra with the reference data from biomass composition, the NIR methods must be calibrated to an accurate primary reference analytical method. For this initial calibration, advanced multivariate models are developed, and although the process cost is slightly increased (30% of the wet chemistry procedure), they are still lower than the wet analysis [1]. Besides, another question raised when building calibration models, is the necessity to have a large variability of the calibration population and of the chemical characteristic of the samples [8].

Most frequently this variability is reached by sampling over different times and locations, what increases the process costs. To avoid such additional costs, some authors have used different botanical fractions from biomass to increase the variability in calibration models [8]. One promising alternative for increasing sample variability would be to use various feedstocks. However, literature [3,8] is scarce on the use of multi-biomass calibration models inwhich one single model combining different biomasses is developed.

According to Liu et al., 2014 themain difficulty in building suchmodels is associated to the dissimilarity among biomasses (different NIR spectra). It is s not practical to develop a NIR calibration model with species showing large dissimilarity. So, to ensure a good prediction and reliable result, principal component analysis (PCA) was performed to justify the development of a single calibration model containing three different biomasses.

Besides, the usual statistical parameters (calibration and validation plots, calibration and validation errors, among others) were used to ensure the confidence of the models.

The objective of this study were to evaluate NIR spectroscopy for measuring the DRC of latex and to establish relationships between the nondestructive NIR spectral measurements and DRC prediction.

Objectives

To evaluate the ability of fourier-transformed near infrared spectroscopy (FT-NIR) to determine dye rubber content (DRC) in field latex

Research Methodology

1. Fresh Latex

The fresh latex were provided by Kalasin province, Northeast of Thailand. Their dye rubber content measured conventionally, spectra of latex were separated in to sample range of 20.0% - 40.0% sample temperature was controlled at 25 °C, calibration set *n* = 90

2. Chemometric analysis of spectral acquisition

Fourier-transformed Transflectance Near Infrared Spectroscopy was operated in the short wavelength region between 400 – 1,100 nm. One spectrum was measured per sample and a reference measurement of Chemometric analyses were conducted using The Unscrambler v10.1 software (Camo Software AS, Oslo, Norway).

2.1 Pre-processing and principal component analysis Vector normalisation (VN), multiplicative scatter correction (MSC) and second derivative were used as pre-processing methods. These pre-processing methods have been successfully applied in similar data obtained for kiwifruit (Chen & Han, 2012; Moghimi et al., 2010). The data were smoothed using Savitsky-Golay method (101 and 35 points for 5990e4250 and 9850e7960 cm^{-1}, respectively) prior to pre-processing to reduce the noise produced during acquisition. Principal component analysis (PCA) was conducted on diffuse reflectance data (n = 300). Through PCA, besides the reduction of the dimension of the variables, the effect on the variance contribution of wavelength (x-variables) and the different data pre-processing methods were assessed. Calibration was performed on n = 210 samples. A randomisation t-test of validation was used to compare the predictive accuracy of the model, by using 30% of the dataset (90 spectra randomly selected).

Selection of a representative calibration sample set. Spectra acquisition and determination of reference values. Multivariate modeling to relate the spectral variations to the reference values of the analytical target property and Validation of the model by cross validation, set validation or external validation. One of the multivariate regression method most frequently used in quantitative NIR analysis is the partial least-squares (PLS) regression, which will be briefly describe in this study

3. Dye rubber content analysis

To calibrate the meter, the correlation between the actual dye rubber content measured by standard laboratory method, ISO126:2005 and A test portion of 10+/-2 g. from a representative sample of latex, accurately weighed by difference, using a 20 ml weighing bottle, is poured into a petri dish having a diameter of 10 cm. The latex is coagulated using a sufficient quantity of acetic acid and heated over a steam bath until a clear serum is obtained before it is pressed with a glass stopper to a uniform thickness not exceeding 2 mm. The coagulum is thoroughly washed and placed in a thermostatically controlled oven at about 65 ^{o}C. After drying rubber is cooled in a desiccator and weighed using an analytical balance. Drying and weighing procedures are continued until the coagulum is dried to a constant weight and the dry rubber content is calculated from the weights of the dry coagulum and the latex sample.

4. Prediction models of calibration equation development

The partial Least Square (PLS) regression method was used to develop calibration models for determining the protein content. The PLS calibrations were performed with the Unscrambler program version 10.1. The optimum number of factors required to minimize over-fitting was based on the standard error of cross validation (SECV). The validation samples set was then used to test the performed calibrations. The standard error of prediction (SEP) and the correlation coefficient of the reference values versus the NIR values(R-pred) were calculated

Prediction models for moisture, soluble solids content, water self-diffusion coefficient and firmness in HB and LB osmodehydrated kiwifruits were developed using partial least squares regressions (PLS). This procedure has been successfully applied for different fruits for the nondestructive assessment of SSC (Arazuri et al., 2005; Chen & Han, 2012; Slaughter & Crisosto, 1998), DM (Qiang et al.,2010; Slaughter & Crisosto, 1998) and firmness (Liu et al.,2011), among other parameters. Individual PLS regressions (PLS1) were conducted by using the spectral acquisitions corresponding to the whole range of wavelengths and the data pre-processing method selected with reference to the results of the PCA. The process of extracting the optimal number of latent variables (LVs), important to avoid over-fitting and under-fitting, was determined by using the minimum value of predicted residual error sum of squares (PRESS). The prediction ability of a model is given as root mean square error of calibration (RMSEC) or prediction (RMSEP) and the correlation coefficient (r) between the predicted and measured value of the attribute. Calibration was performed by using the 70% of the dataset (210 spectra randomly selected), while the randomisation t-test of validation was used to compare the predictive accuracy of models, by using the 30% of the dataset (90 spectra randomly selected). The values of PRESS, RMSEC and RMSEP were calculated using the equations from the literature (Chen & Han, 2012; Liu et al., 2014; Qiang et al., 2010). Only three samples were excluded as outliers for all the predictions, considering their high leverage and high residual Xvariance. The accuracy of the predictive model was also studied by calculating the residual predictive deviation (RPD) obtained by dividing the standard deviation (SD) of the reference values by the SEC (square error of calibration) (Williams & Norris, 2001).

Result and Discussion

Fig. 1 shows the raw spectra of the fresh latex were provided by Kalasin province and different to determine dye rubber content (DRC) in field latex, samples were measured in the long wavelength region (1000 nm – 2495 nm) the sample range of 20.0% to 40.0% sample temperature was controlled at 25 °C.

Conclusion

Using PLS methods to develop the models of this study, the best results are r = 0.89, RMSEC = 4.09 N for calibration and r = 0.57, RMSEP = 6.57 N for validation, using the original spectra of 64 scan number and 2 cm–1 resolution without preprocessing. The results show that kiwifruit firmness prediction by NIR diffuse reflectance is feasible. The handheld NIR spectrometer could be used as a Dry Rubber Content analyzer to predict DRC accurately for price determination for Latex trading, a spectral acquisition system of a single sample should be used.

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Table 1

Descriptive Statistics for dry rubber content in field latex samples.

	Mean	SD	Range	CV
Calibration	33.31	6.35	20.62 - 40.75	19.06
Predicted value	33.44	6.16	22.73 – 39.52	19.03

Table 2.

Characteristics of calibration and validation sample sets of DRC in fresh Latex used.

	F	R^{2*}	SEC	SEP	*Bias*
Calibration	5	0.99	0.18	-	0.000
Validation	5	0.98	-	0.99	0.029

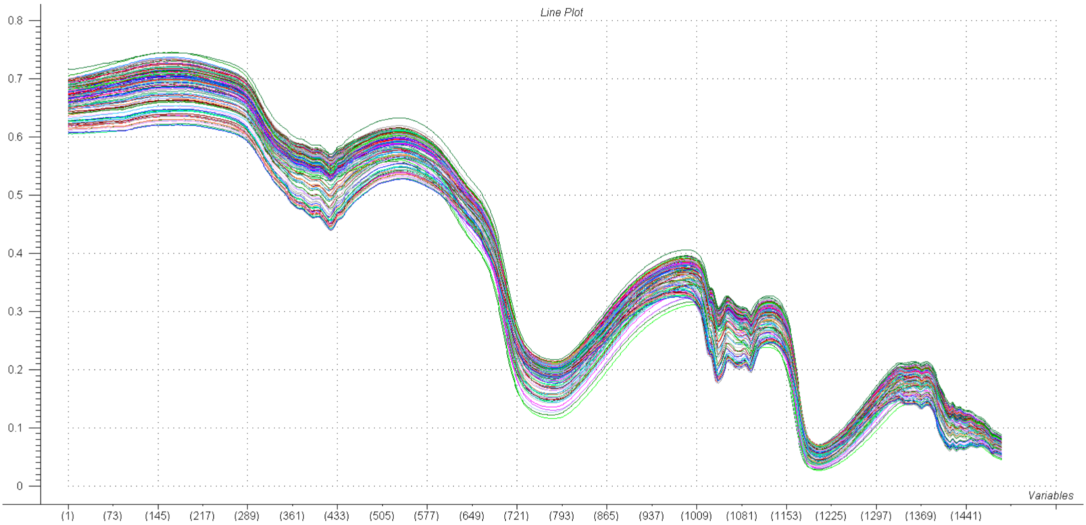

Figure 1 initial spectra of calcium chloride content in rubber cublum with different moisture content

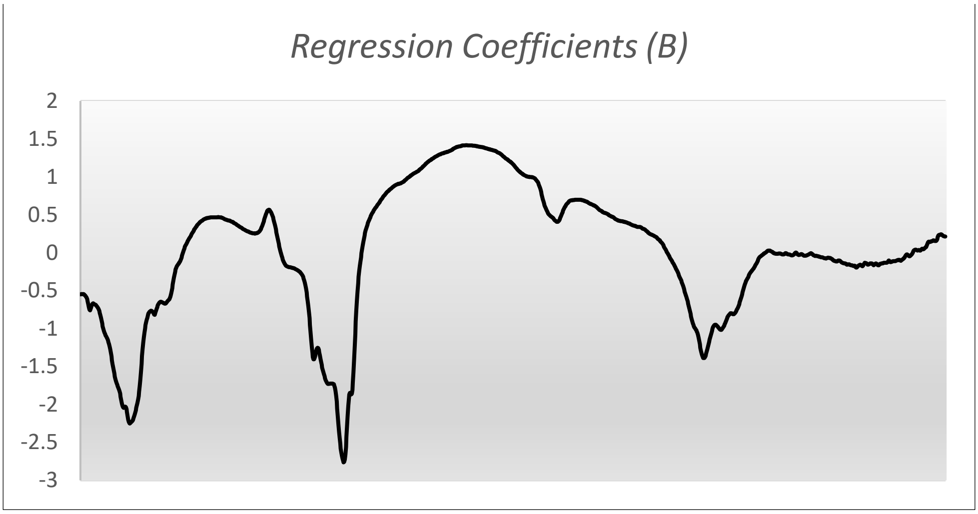

Figure 2 Second derivative spectra of calcium chloride content in rubber cublum with different moisture content

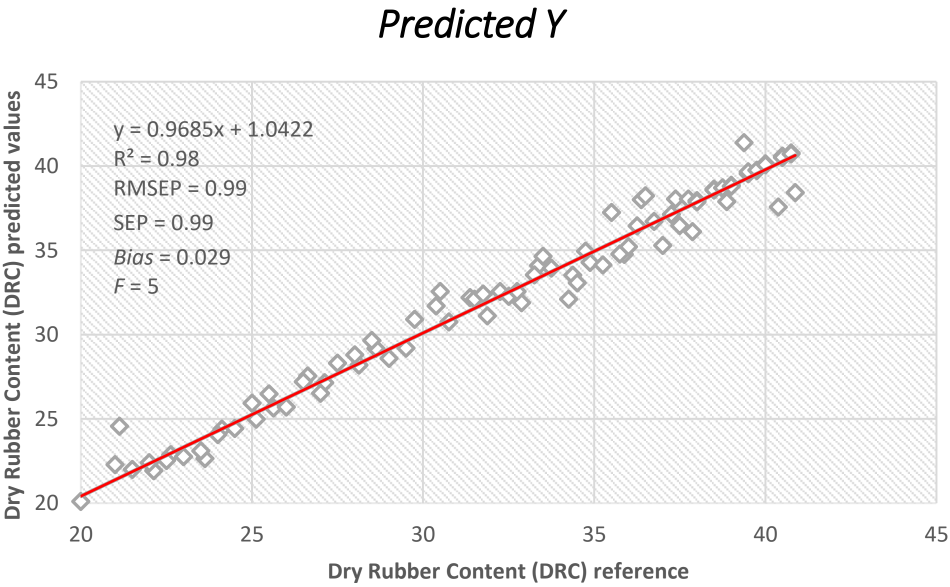

Figure 3 (a) The analysis results of PLS regression coefficients for calcium chloride in rubber cublum using the data adjusted by smoothing technique and second derivative technique under the light frequencies ranging between 4000 – 8000 cm^{-1}

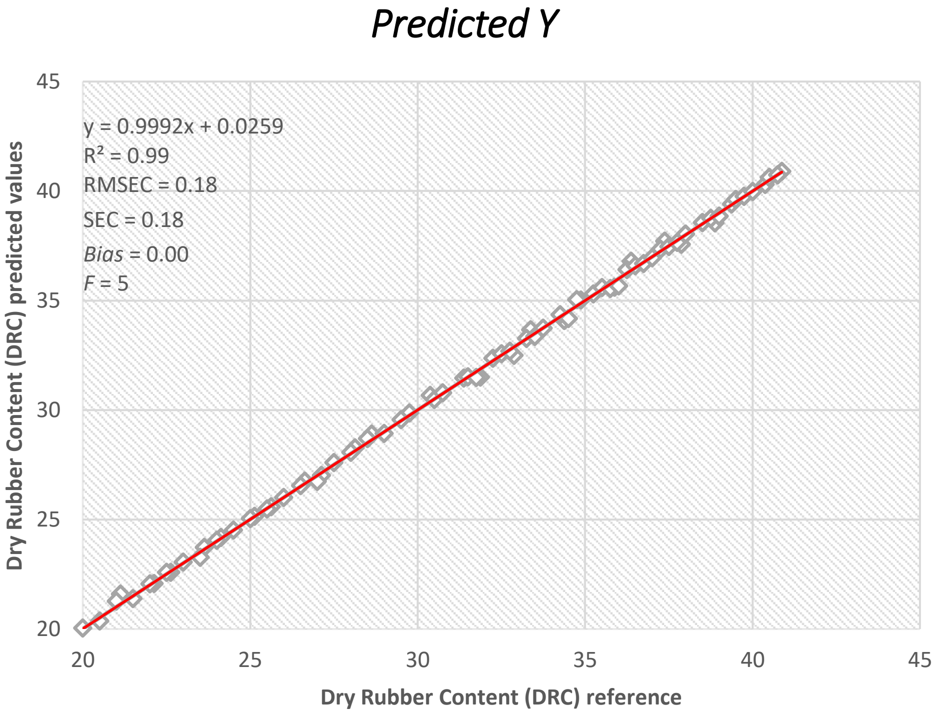

Figure 4 (b) The analysis results of PLS regression coefficients for calcium chloride in rubber cublum using the data adjusted by smoothing technique and second derivative technique under the light frequencies ranging between 4000 – 8000 cm^{-1}