

Moisture content analyzer for raw rubber sheet by handheld near infrared spectrometer

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Introduction

Rubber is an important material for multiple applications, particularly in the expanding automobile industry. Thailand is the world's number one natural rubber producer and exporter. In 2008, its production volume was approximately 3.1 million tons, of which 88 % were exported and the rest was distributed domestically.

In Thailand, with the current system for trading raw rubber sheet, the prices paid to rubber farmers are adjusted according to the moisture content. The rubber moisture content is estimated principally by the visual method and by touching of the raw rubber by the examiner. The result can be affected by environmental factors, and by the personal expertise of the examiner (trader). This places the rubber farmers at a possible disadvantage. For example, based on the total volume of rubber sheet annually produced in Thailand, if the trader over- or under-estimates the moisture content by only 1 % this could result in the loss of 1.8 billion baht (about \$55 million) per year by the farmers or the traders. Therefore, an accurate and rapid moisture measurement system is required to make fair trading for both traders and farmers.

As a possible alternative, near-infrared (NIR) spectroscopy is widely used for quantitative analysis of moisture content. The technique has been used, for example, on triticale,¹ brown rice kernels,² corn kernels,³ wheat and barley.⁴ Therefore, NIR spectroscopy is a suitable method for quantifying trace amounts of moisture in raw rubber sheet, due to the strong combination absorption bands for water at around 1940 nm and the first, second, and third overtones at 1450 nm, 970 nm and 760 nm, respectively. However, there has been little research into the prediction of moisture content in raw rubber sheet. This study presents the development of a NIR method for measuring moisture in raw rubber sheet, and the comparison of the accuracy of spectrum acquisition systems, between using a single sheet, and a pile of sheets.

Materials and Methods

Raw rubber sheet

Raw rubber sheets were provided by Northeast Rubber Company, Buriram Province, Thailand. They were divided into two groups; one hundred and forty samples for the calibration sample set, and one hundred and twenty five samples for the validation sample set.

Spectral acquisition

The spectrum of raw rubber sheet was measured by a handheld NIR spectrometer (FQA-NIRGUN, Fantec, Japan), operating in the short wavelength region (700–1100 nm) in the interactance mode with calculation time of 6 ms.

Moisture content analysis

Moisture content was determined by drying the raw rubber sheet in a hot air oven at 100 °C for 10 h. Moisture content was reported directly.

Calibration equation development

Prior to developing a calibration, the spectra were pretreated with the second derivative (segment size 16 points and derivative size 12 points). CA maker software (Shizuoka Shibuya Seiki, Hamamatsu, Japan) was used to perform multiple linear regressions (MLR).

Results and discussion

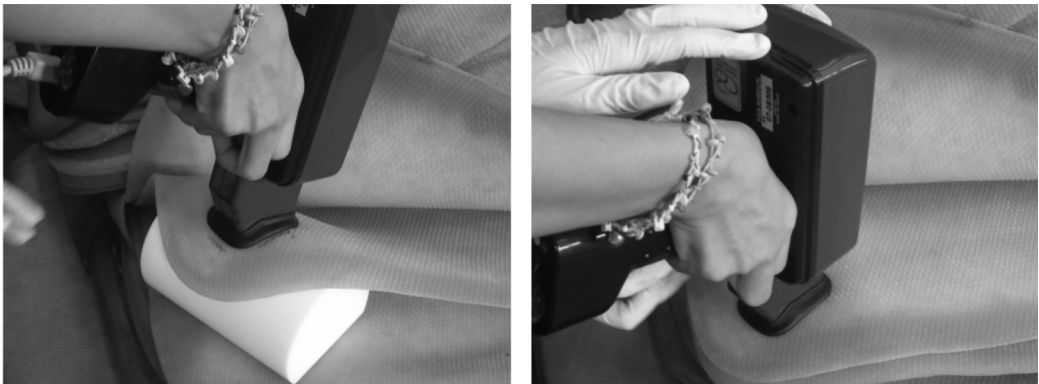
Spectral acquisition testing

Spectra acquisition system of raw rubber sheet was tested by placing a measuring head in direct contact with the surface of the sheet, using one sheet for the single sheet system and several sheets for a pile of sheets system. Due to the translucent property of the rubber sheet, and the power of the light source, the light reflected to the detector was too intense and the handheld spectrometer in the interactance mode was not able to measure a spectrum of a single sheet effectively. Therefore, the measuring system was modified to the transreflectance mode, using a material serving as diffuse reflector for reflecting energy to the detector.

For this purpose, Teflon, a material having a constant optical property and practically no absorption in the NIR region, was selected. The curved Teflon block, designed especially for use with raw rubber sheet, and the FQA-NIRGUN, was built with a smooth surface and a radius of 4.5 cm, in order to make the measuring head fit perfectly to the rubber sheet. It was placed under a single rubber sheet before measuring the spectrum as shown in Figure 1(a). For measuring the spectrum of a pile of rubber sheets, the measuring head was pressed onto the uppermost rubber sheet [Figure 1(b)].

NIR spectra of raw rubber sheet

Baseline shifts occurred (Figure 2) due to the differences in each rubber sheet thickness. The peak of isoprene, the major component of rubber sheet, could be observed around 900 nm,



(a) (b)
Figure 1. Spectral acquisition system of raw rubber sheet with Teflon under (a) a single rubber sheet and (b) a pile of sheets

which is the absorption of CH_3 and CH_2 third overtones of isoprene. Consequently, the spectra were pretreated with second derivatives to remove the baseline shift effect. After pretreatment, the spectra were close to each other showing that the effect of baseline shift had been removed.

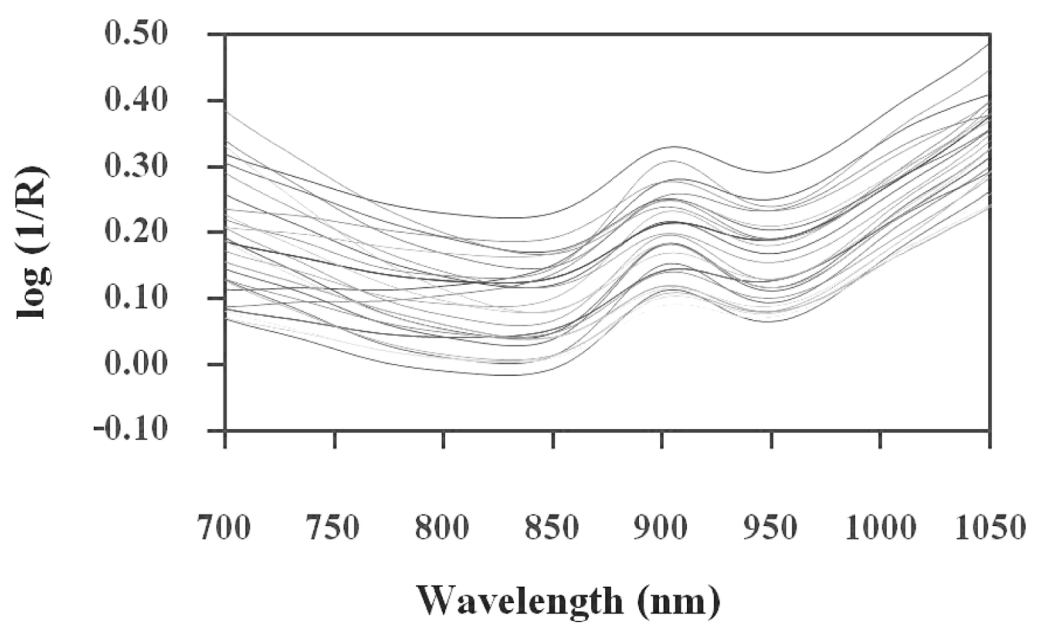


Figure 2. Original spectra of raw rubber sheet in the short wavelength region.

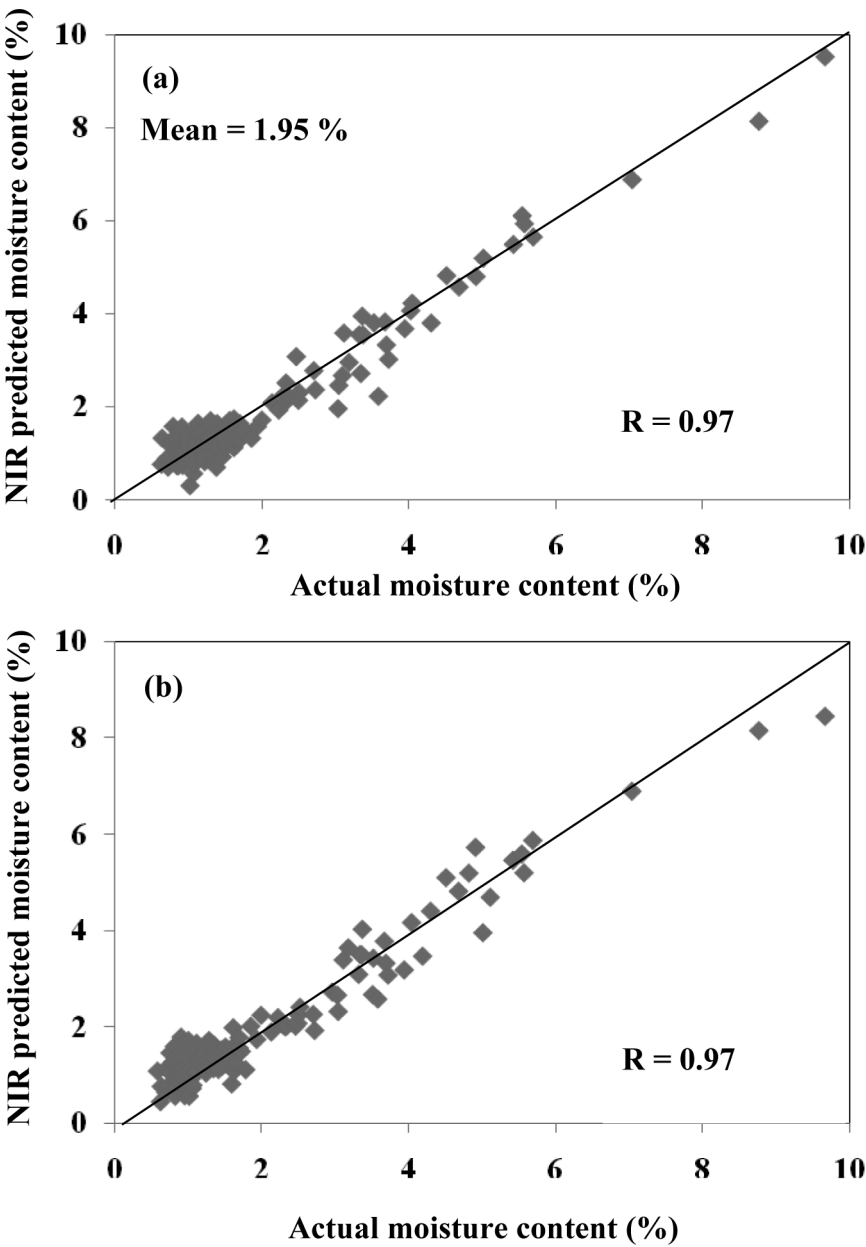


Figure 3. (a) Scatter plots of a single sheet system, $SD = 1.57\%$ below $Mean = 1.95\%$ and $SEC = 0.37\%$ below $R = 0.97$ and (b) a pile of sheets system, $SEC = 1.08\%$ below $R = 0.97$, in the calibration set.

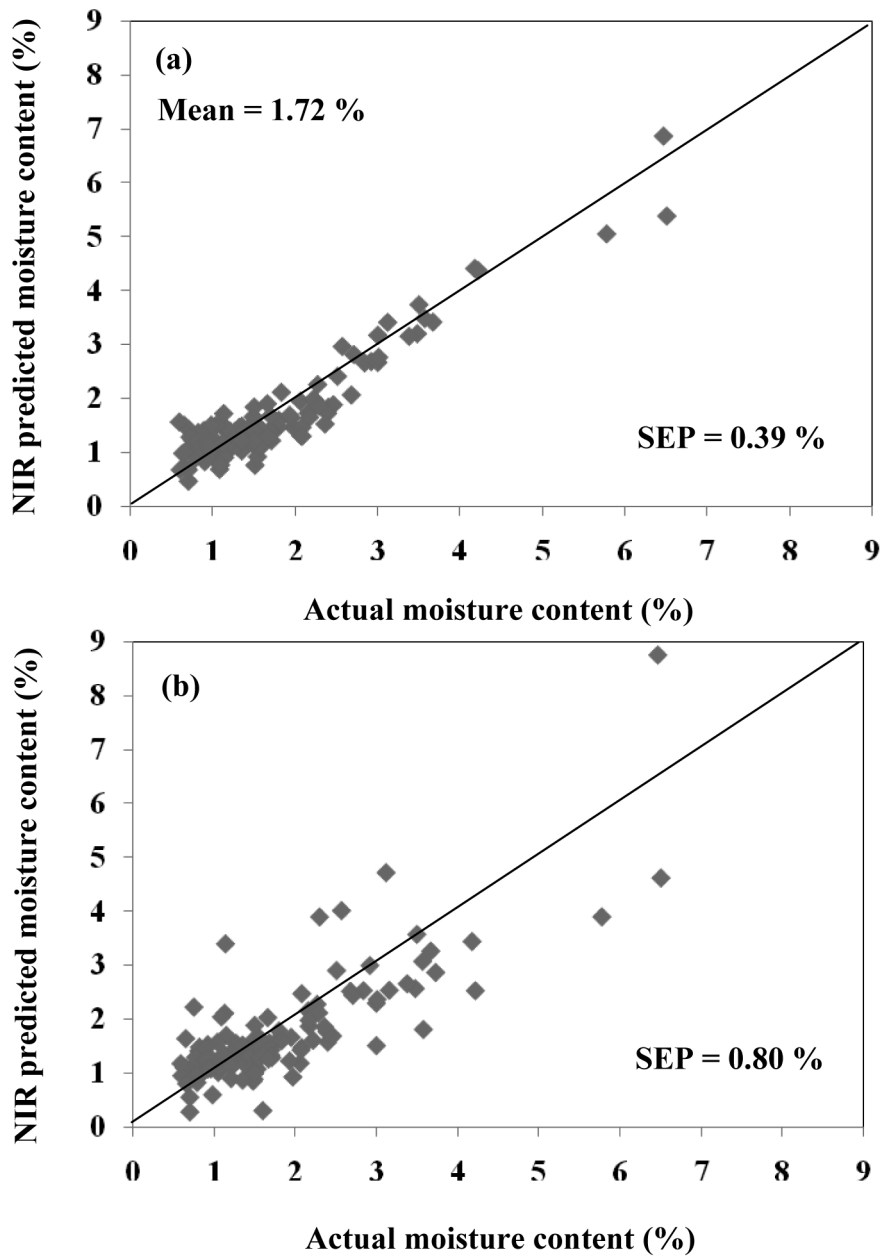


Figure 4. (a) Scatter plots of a single sheet system, $SD = 1.08\%$ below Mean = 1.72% and Bias = 0.07% below $SEP = 0.39$ and (b) a pile of sheets system, Bias = -0.14% below $SEP = 0.80\%$, in the validation set.

Calibration equation development

The results of calibration equations of moisture content are shown as scatter plots (Figure 3). Dots scattered close to the target line indicated that the predicted values were close to the actual ones. In the single sheet analysis, the multiple correlation coefficients (R) and the standard error of calibration (SEC) were 0.97 and 0.37 % respectively, while they were 0.97 % and 0.41 % in the pile of sheets analysis.

For accuracy comparison, the validation set was used to test the accuracy of both calibration equations. The result in Figure 4 revealed that moisture content predicted by the single sheet system was more accurate than that of the pile of sheet system, with standard error of prediction (SEP)=0.39 % and bias of -0.07 %. Using the paired t-test of the calibration equation in the single sheet system, moisture contents predicted by NIR were not significantly different from the actual values at the 95% confidence level.

Because of the translucent property of rubber sheets in a pile of sheets system, an NIR spectrum was an average absorbance of three to four sheets, the moisture content of the top sheet only was measured and used for calibration development. Therefore, the spectrum collected from a pile of sheets did not correspond closely to the measurement of moisture content. In the single sheet system, Teflon was placed under each sheet, so that a spectrum was collected from only one sheet, and the absorbance of that sheet was used to predict moisture content. Finally, an MLR moisture calibration equation developed by single sheet analysis was as follows;

$$\text{Moisture (\%db)} = 0.7637 - 60.3342A_{728} + 384.8081A_{860} - 342.9129A_{956} - 126.3390A_{984} + 55.1054A_{1040}$$

where, A is second derivative of an absorbance at the wavelength of x nm.

From the above equation, the most important wavelength in the equation is 956nm, which is related to water absorption.

Conclusion

A handheld NIR spectrometer could be developed to be a moisture content analyzer for analysis of rubber sheets. To predict moisture content accurately for price determination for raw rubber sheet trading, spectral acquisition system of a single sheet should be used.

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