Quantitative analysis of quality for marian plum *(Boueaburmanica Griff.)* by transmittance near infrared spectroscopy

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Abstract

Marian plum *(Boueaburmanica Griff.)* is one of the most popular tropical fruits in Thailand. The good quality of marian plum is required by consumers. Total soluble solid (TSS) and titratable acidity (TA) are the important indices for consideration of quality for marian plum. Transmittance mode of near infrared (NIR) spectroscopy in the short wavelength (665–955 nm) was considered for nondestructive evaluation of quality in marian plum. A set of 153 marian plums (105 samples for a calibration group and 48 samples for a prediction group) was carried out in this research. The Partial Least Squares Regression (PLSR) was used to develop the calibration models. Spectral pretreatments were investigated in order to obtain the best performance of the models. A calibration model for TSS using original spectra obtained best results for calibration and prediction (R=0.90, RMSEC=0.57 °Bx and R=0.88, RMSEP=0.65°Bx, respectively). As well as the calibration model for TA using original spectra obtained best results for calibration and prediction (R=0.98, RMSEC=0.01% and R=0.88, RMSEP=0.03%, respectively). All results indicated that it is possible to use transmittance SW-NIRS for nondestructive prediction of TSS and TA in marian plums.

Keywords: nondestructive, total soluble solid, titratable acidity and prediction

Introduction

Marian plum *(Boueaburmanica Griff.)* is one of tropical fruits that play a significant role in the Thai economy. Agriculturists tend to grow and sell marian plums to both domestic and international market. The fruit can be sold at a high price because of its uniqueness in delicious taste and can be grown only in specific area. However, there has been a controversy about the accepted quality of the marian plums among agriculturists, middlemen, and consumers. Therefore, quality control is needed to determine the qualities of fruits before supplying to the market. Traditionally, it is common to destruct marian plums during the quality control process; therefore, nondestructive techniques are required to do for a real practice. NIR Spectroscopy was one of the reliable techniques which bring to used for quality assessment of fruit (Osborne et al., 1993, Walsh et al., 2004). Absorption energy of molecular bond due to the vibration occurred in NIR wavelength is investigated in NIR technique. Therefore, samples of marian plum do not need to be destructed.

Due to there were many reports presented that the short wavelength near infrared (SW-NIR) spectroscopy was able to accurately predict for internal quality of fruit (Teerachaichayut et al., 2007, Teerachaichayut et al., 2011, Sukwani et al., 2013, Jannok et al., 2014, Teerachaichayut et al., 2014). Therefore, this study was designed to examine the equations for predicting total soluble solid (TSS) and titratable acidity (TA) of marian plums by applying the transmittance NIR spectroscopy technique in the range of short wavelength between 800-1100 nm. Ultimately, the data from this study will be used to identify the quality of marian plums by nondestructive based technique.

Meterials and Mothods

Sample preparation

Samples were selected by inspection for the same size (about 100 g each) with good appearance. We obtained a set of 153 marian plums that were grown in Nakornnayok, Thailand. The samples in the orchard needed to be waited for 70-75 days after blooming to ensure its maturity for harvest. Each marian plum was carefully transported to the laboratory and kept in a air-conditioned room (25 °C) about 24 hr. before measurement.

Spectra acquisition

In order to identify the absorption spectra, the samples were measured by Short Wavelength Near Infrared (SW- NIR) spectrophotometer (PureSpect, Japan) in transmittance mode with short wavelength between 665-955 nm. For each sample, there were four scanned points at equator of each fruit that were manually rotated every 90° each.

Method of Measurement

The samples were weighted by using a digital scale (SDS, IDS 704, Japan), then they were taken to measure the absorbance spectra by transmittance SW-NIR spectrophotometer at the four identified areas, then an averaged spectrum of each sample was calculated and used for analysis. After that the skin of each sample was peeled, then the pulp was cut and squeezed, and finally, it was filtered to receive the marian plum juice. In addition to the preparation of the samples, the juice was separated into two parts. The juice from the first part was measured TSS using a digital hand refractometer (ATAGO, PAL-1, Tokyo) which showed the value in °Brix. Titration was carried out according to the standard method described by AOAC (2000) to measure TA that obtained from the second part of the juice.

Data analysis

Partial Least Squares Regression (PLSR) was employed to determine the relationships between chemical components and averaged spectrum of the samples. Unscrambler program (CAMO, Oslo, Norway) was used for statistical analysis. Data were divided into two groups: (1) the calibration set, used to establish PLSR models between the dependent variables (TSS and TA) and the independent variables (averaged spectra in the short wavelength between 665-955 nm), and (2) prediction set, used to measure efficiency or capability of prediction when the PLSR models were tested. In addition, the prediction set was not involved in establishment of the PLSR models.

Initially, several pretreatment techniques, including: smoothing, first derivative, second derivative, multiplicative scatter correction MSC were applied to original spectra or absorbance or log (1/R) before establishment of the PLSR models. As the results, there were investigated to find out the best conditions for the models. By considering of correlation coefficient (R) and Root Mean Square Error of Cross-Validation (RMSECV), the most effective equations for TSS and TA were selected for this study. Then we used the equations to test in the prediction set and evaluate the efficiency of the models by consideration of correlation coefficient (R) and Root Mean Square Error of Prediction (RMSEP).

Results and discussion

In Figure 1, it showed averaged spectra of samples (N=153) at wavelength range of 665-955 nm in this experiment.

Analysis of Total Soluble Solid (TSS)

In Table 1, TSS from a set of 153 marian plums were measured. The samples were selected and categorized into two groups: (1) calibration set, which accounted for 105 samples, and (2) prediction set, which accounted for 48 samples. Then, the wider range of TSS (17.60-25.40 °Bx) in the calibration set were used for development of the PLSR model by absorbance spectra in short wavelength between 665-955 nm Furthermore, the predictive accuracy of the model was evaluated by the TSS (17.90-24.60 °Bx) in the prediction set.

In Table 2, after manipulating by applying various mathematics methods for spectral pretreatments, the original spectra by cross-validation showed the best results (R=0.88, RMSECV=0.64 °Bx) for TSS. Therefore, the original spectra were used for establishment of the PLSR model for TSS.

In Table 3, as a consequence, PLSR model for TSS was acquired from original spectra and then cross validated. The results from the calibration set obtained R=0.90 and RMSEC=0.57 °Bx. Moreover, the PLSR model for TSS was used in the prediction set. The predictive results showed R=0.88 and RMSEP=0.65 °Bx.

Analysis of Titratable Acidity (TA)

In Table 4, the same method of evaluation as TSS was done for TA. TA from a set of 145 marian plums were assessed. The samples were classified for the calibration set (N=102) and the prediction set (N=43). The ranges of TA were 0.22-0.6% and 0.22-0.57%, respectively.

In Table 5, spectral pretreatments were investigated, the original spectra by cross-validation showed the best results (R=0.89, RMSECV=0.04%) for TA. Hence, the original spectra were used for establishment of the PLSR model for TA.

In Table 6, acquired PLSR model for TA was carried out for prediction. The results of the calibration obtained R=0.98 and RMSEC=0.01%. Furthermore, the PLSR model for TA was performed in the prediction set. The predictive results showed R=0.92 and RMSEP= 0.03%.

Both of PLSR models for TSS and TA were developed by using original spectra of marain plum. In Figure 2, the scattered plots between the measured values and predicted values in the calibration set and the prediction set were presented. Results of prediction for TSS and TA in the calibration set by cross validation and in the prediction set were shown in Figure 2(a) and 2(b), respectively.

Conclusion

Original spectra were used for establishment of PLSR models for TSS and TA. The statistic results presented that the PLSR models for both of TSS and TA were satisfied to use for quality prediction of marian plum. Therefore, the transmittance NIR spectroscopy technique in the short wavelength (665-955 nm) has a potential to use for nondestructive determination of TSS and TA in intact marian plum.

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Tables

Table 1. Characteristics of variables in the calibration and prediction set for TSS.

Items	The calibration set	The prediction set
number of samples	105	48
mean	22.14	22.06
minimum	17.60	17.90
maximum	25.40	24.60
standard deviation (SD)	1.37	1.39
unit	°Brix	°Brix

Table 2. Spectral pretreatments for establishment of the PLSR model for TSS.

Spectral pretreatments	N	F	R	RMSECV	Wavelength
original	105	7	0.88	0.64	665-955 nm
smoothing	105	8	0.88	0.65	665-955 nm
1st derivative	105	8	0.87	0.67	665-955 nm
2nd derivative	105	8	0.87	0.66	665-955 nm
MSC	105	10	0.87	0.67	665-955 nm
Mean	105	13	0.87	0.68	665-955 nm
SNV	105	12	0.87	0.67	665-955 nm
smoothing + 1st derivative	105	11	0.87	0.67	665-955 nm
smoothing + 2nd derivative	105	5	0.88	0.64	665-955 nm
MSC + Smoothing + 1st derivative	105	9	0.85	0.72	665-955 nm
MSC + Smoothing + 2nd derivative	105	9	0.85	0.71	665-955 nm
mean + Smoothing + 1st derivative	105	10	0.87	0.67	665-955 nm
mean + Smoothing + 2nd derivative	105	10	0.87	0.67	665-955 nm
SNV+ Smoothing + 1st derivative	105	11	0.84	0.72	665-955 nm
SNV+ Smoothing + 2nd derivative	105	7	0.85	0.72	665-955 nm

N= number of sample
F = factors
R= correlation coefficient

RMSECV= root mean square error of cross validation
Smoothing = Savitzky-Golay smoothing
1st derivative = Savitzky-Golay first derivative
2nd derivative = Savitzky-Golay second derivative
MSC = multiplicative scatter correction pretreatment
Mean = mean center
SNV = standard normal variate transformation

Table 3. Results of PLSR model for TSS.

Items	The calibration set	The prediction set
Spectra	Original	Original
N	105	48
F	7	7
R	0.90	0.88
RMSEC/RMSEP	0.57	0.65

Table 4. Characteristics of variables in the calibration and prediction set for TA.

Items	The calibration set	The prediction set
number of samples	102	43
mean	0.35	0.36
minimum	0.22	0.22
maximum	0.60	0.57
standard deviation (SD)	0.07	0.08
unit	%	%
wavelength	665-955 nm	665-955 nm

Table 5. Spectral pretreatments for establishment of the PLSR model for TA.

Spectral pretreatments	N	F	R	RMSECV	Wavelength
original	102	16	0.89	0.04	665-955 nm
smoothing	102	8	0.73	0.04	665-955 nm
1st derivative	102	8	0.73	0.04	665-955 nm
2nd derivative	102	7	0.77	0.04	665-955 nm

Spectral pretreatments	**N**	**F**	**R**	**RMSECV**	**Wavelength**
MSC	102	10	0.78	0.04	665-955 nm
Mean	102	9	0.78	0.04	665-955 nm
SNV	102	14	0.79	0.04	665-955 nm
smoothing + 1st derivative	102	7	0.74	0.04	665-955 nm
smoothing + 2nd derivative	102	8	0.73	0.04	665-955 nm
MSC + Smoothing + 1st derivative	102	9	0.74	0.04	665-955 nm
MSC + Smoothing + 2nd derivative	102	7	0.72	0.05	665-955 nm
mean + Smoothing + 1st derivative	102	9	0.73	0.04	665-955 nm
mean + Smoothing + 2nd derivative	102	9	0.72	0.04	665-955 nm
SNV+ Smoothing + 1st derivative	102	6	0.74	0.04	665-955 nm
SNV+ Smoothing + 2nd derivative	102	7	0.73	0.04	665-955 nm

N= number of sample
F = factors
R= correlation coefficient
RMSECV= root mean square error of cross validation
Smoothing = Savitzky-Golay smoothing
1st derivative = Savitzky-Golay first derivative
2nd derivative = Savitzky-Golay second derivative
MSC = multiplicative scatter correction pretreatment
Mean = mean center
SNV = standard normal variate transformation

Table 6. Results of PLSR model for TA.

Items	**The calibration set**	**The prediction set**
Spectra	Original	Original
N	102	43
F	16	16
R	0.98	0.92
RMSEC/RMSEP	0.01	0.03

Figures

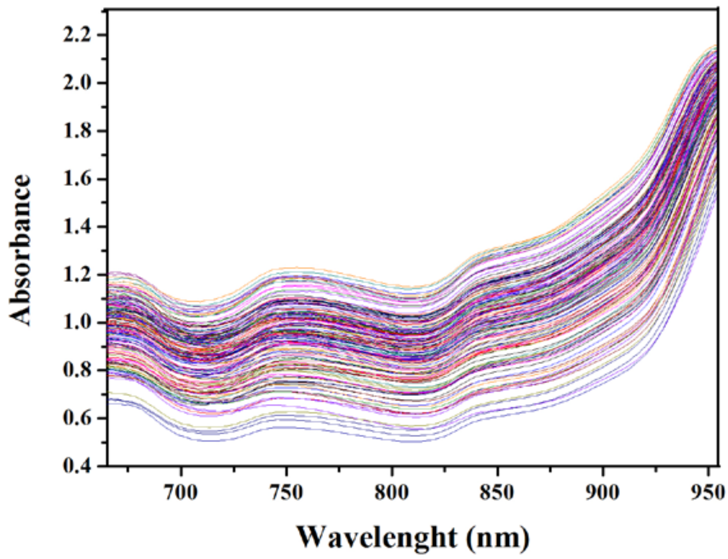
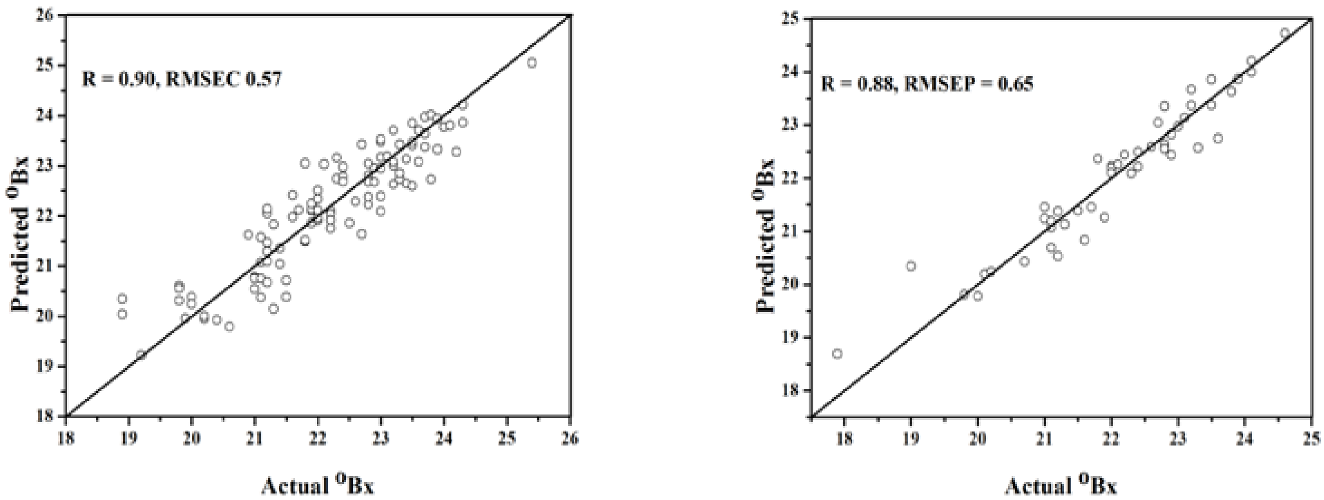
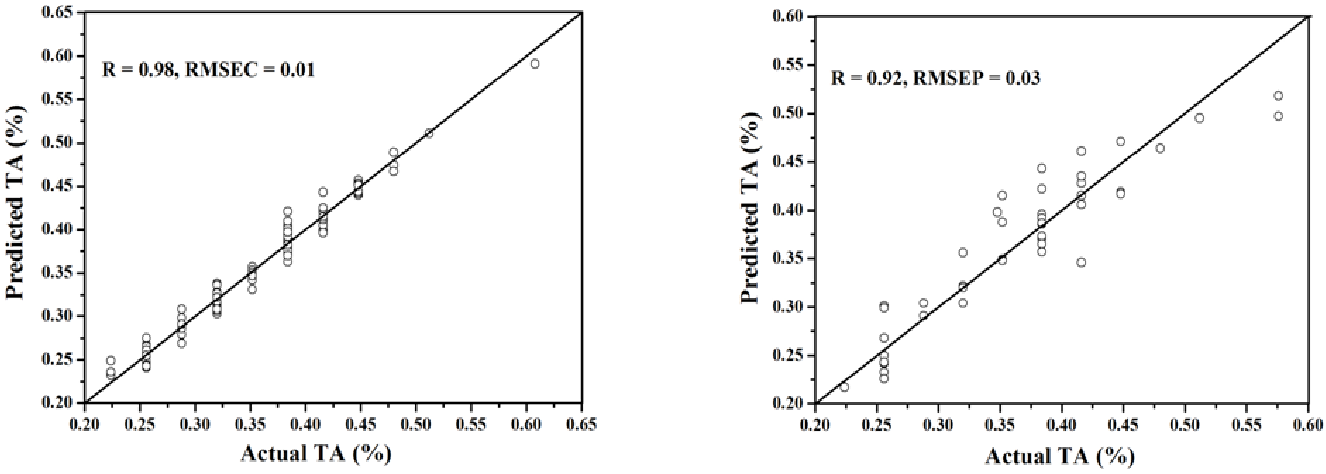


Figure 1. Averaged original spectra of marian plums.



(a)



(b)

Figure 2. Scattered plots of PLSR models for the calibration set and the prediction set: (a) for TSS (b) for TA.