

Use of peel spectral information to improve titratable acidity prediction in intact tangerine by near infrared spectroscopy in long wavelength region

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Introduction

Prediction of titratable acidity (TA) content in several fruit including citrus by NIRS is limited due to relatively low amount of organic acids in fruit. A model developed based on visible/NIRS spectroscopy, equipped with a post-dispersive reflectance configuration, showed unacceptable accuracy for TA prediction in oranges cv. Valencia Late.¹ However, good calibrations were obtained for TA prediction in intact Imperial mandarin² and Satsuma mandarin fruit.³ The presence of the fruit skin or peel has been known to decrease the performance of calibration models. The fruit skin was found to act as a barrier for light penetration into mandarin fruit.⁴ In another report, the best models for soluble solids content (SSC) and dry matter content were achieved for intact Imperial mandarin using NIR spectra of whole fruit with the skin removed.⁵ There has been a report on a technique for elimination of peel interference in visible/NIR spectroscopy for nondestructive determination of internal quality of fruit and vegetables.⁶ The flesh optical density of potato can be predicted nondestructively using the whole potato transmittance and the diffuse reflectance measurements at the irradiated site and the opposite site where the light is transmitted.

This research studied use of spectral information of peel in improving prediction of titratable acidity (TA) of thin-peel fruit in tangerine by near infrared spectroscopy in the long wavelength region.

Materials and methods

Samples

Two hundred and four tangerines of “Sai-Num-Pung” (meaning honey) variety were selected from a local market. They were transported to the air-conditioned laboratory room where they were kept overnight at 25°C prior to data collection.

Near infrared measurements

Diffuse reflectance spectra of tangerine samples were recorded using an InfraAlyzer 500 instrument and dedicated SESAME software version 2.00 (Bran and Luebbe GmbH, Norderstedt, Germany) in a wavelength range between 1100 and 2500 nm at 2 nm intervals. The spectral measurements were made at two opposite points on an equatorial line of the fruit. They were averaged and used as a mean spectrum of each fruit for further analyses. Each sample was then peeled and rescanned at the same sites to collect the corresponding spectra of peeled fruit. Similarly, the mean spectrum as an average of two measurements was used for the peeled samples.

Total acidity analysis

Traditional destructive tests were used to determine TA. Each fruit unit was juiced and a 2 mL sample of juice diluted to 10 mL was titrated against standard NaOH 0.1 N until phenolphthalein indicator changed to pink color. TA value was expressed as percentage in terms of the citric acid equivalent as follows:

$$\text{Acidity (\%)} = \frac{N \times T \times 0.064 \times 100}{V}$$

where N is the normality of titrant, T is the volume of titrant and V is the volume of the sample. Milliequivalent of citric acid (anhydrous) is equal to 0.064.⁷

For each fruit, an average value of three replicates was obtained for all measurements.

Development of near infrared (NIR) models

For model development, all samples were divided into two sets in which similar distribution of the chemical value (Table 1) was obtained. The first set of 133 spectra, designated as a calibration set, was used to develop a partial least squares regression (PLSR) model with Unscrambler 9.8 (CAMO, Norway). Second derivative (2D) was selected for pretreatment of the raw spectra before building the models, and they were investigated in conjunction with PLSR modeling. Full cross validation was applied to determine the optimal number of factors for the calibration model. Predictive performance of the PLSR model was assessed on prediction of data in an independent validation set (67 spectra taken from one of every four samples in the initial set).

Table 1. Number of samples, maximum value, minimum value, mean and standard deviation of tangerines for the analyses.

| | Total acidity (%) | |
|--------------------------|-------------------|------------|
| | Calibration | Prediction |
| No. of samples | 133 | 67 |
| Maximum value | 0.31 | 0.34 |
| Minimum value | 0.98 | 0.90 |
| Mean | 0.55 | 0.54 |
| Standard deviation | 0.14 | 0.13 |
| Coefficient of variation | 25.45% | 24.07% |

Results and discussion

Fruit quality properties

A summary of statistics of data in a calibration and validation sets is presented in Table 1. A reasonably good range of TA was obtained.

NIR absorbance spectra

Averaged spectra of intact and peeled tangerine are presented in Figure 1 for the wavelength region from 1100 to 2500 nm. The intact tangerine spectrum showed distinct water peaks at around 1425 and 1940 nm. The peeled tangerine spectrum on the other hand did not show clearly any characteristic peaks over all wavelengths. This would probably be caused by high light scattering on rough surface of the peeled tangerine.

Prediction of total acidity

Predicting performance for TA in the intact tangerine was given as SEP of 0.097% and bias of -0.009%.

It was hypothesized that the prediction could be improved if the variation of peel absorbance was reduced between samples.

Spectral information in association with the tangerine peel

Arbitrary investigation was thus performed to extract spectral information associated with the peel. Such spectral information would be used to adjust the raw spectra of intact tangerine in calibrating the model. The raw absorbance spectra of both intact and peeled tangerine were subjected to partial least squares discriminant analysis (PLS-DA). The principal components (PC) that contributed to discrimination between both groups of samples would contain spectral information associated with the peel. High x-loading weights of the PC were explored to indicate the wavelengths at which the absorbance of the intact tangerine was different from the peeled tangerine, hence the peel wavebands.

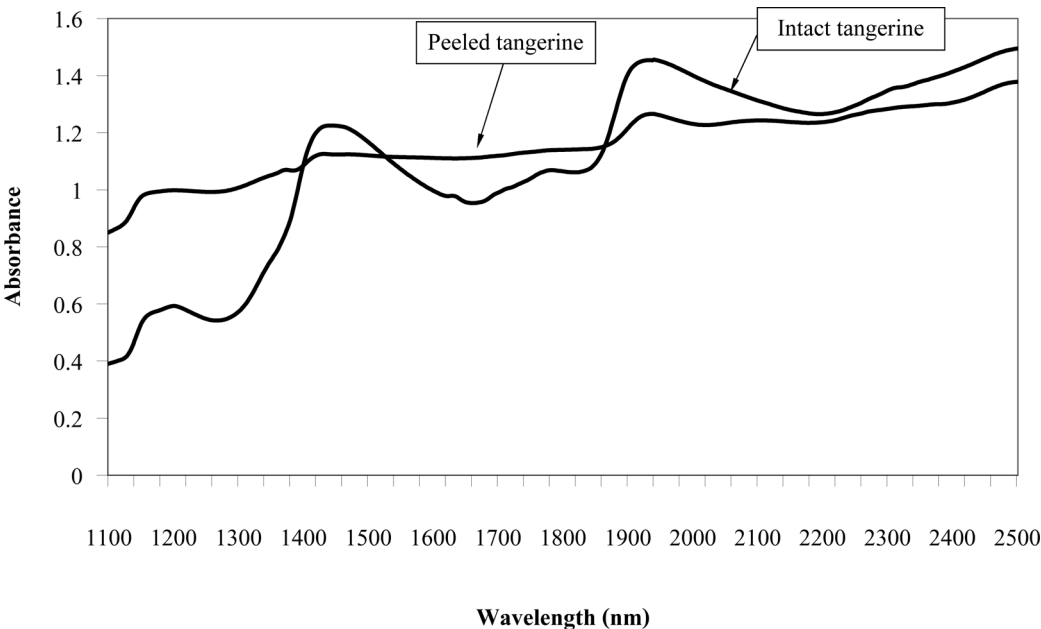


Figure 1. Averaged absorbance of intact and peeled tangerines.

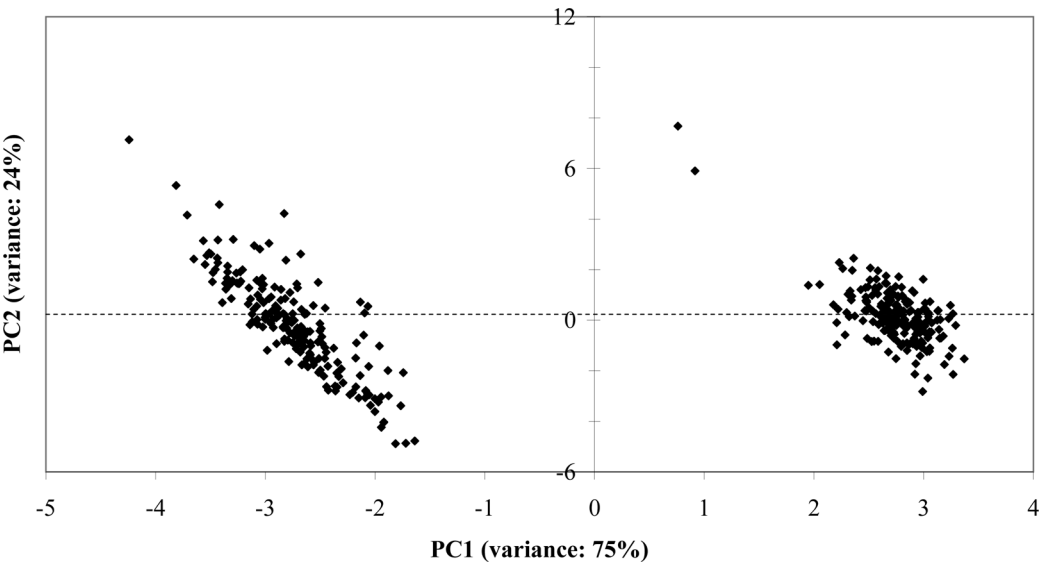


Figure 2. Score plot of partial least squares discriminant analysis between intact orange (left group) and peeled orange (right group).

Table 2. Prediction results of titratable acidity in intact tangerines using PLS models based on original and normalized spectra.

| | Pretreatment | <i>F</i> | <i>R</i> _{cal} | <i>SEC</i> | <i>R</i> _{pre} | <i>SEP</i> | BIAS | <i>RMSEP</i> |
|------------------------|-------------------|----------|-------------------------|------------|-------------------------|------------|--------|--------------|
| Original spectra | Second derivative | 10 | 0.744 | 0.092 | 0.662 | 0.097 | −0.009 | 0.096 |
| A_λ/A_{1654}^* | Second derivative | 14 | 0.912 | 0.056 | 0.823 | 0.076 | −0.007 | 0.076 |

* Normalized by dividing absorbance (A_λ) with absorbance at 1654 nm (A_{1654})

The peel associated wavebands were used to normalize and center the intact tangerine raw spectra prior to the pretreatment and PLS model development. Such adjustments of the raw spectra were aimed to diminish variation of the peel absorbance inherent in the raw spectra.

The score plot obtained in PLS-DA illustrated clearly the separation between the intact tangerine samples and the peeled ones (Figure 2) by PC1 (explained variance of 75%).

Three regions of high loading weights i.e. 1128–1144, 1262–1278 and 1654–1672 nm were selected and used in modification of the raw spectra for the recalibration of the PLS models. The raw spectra normalization by each individual wavelength was investigated as part of model calibration. Table 2 shows the best model for predicting TA that was built on normalized raw spectra. It was found that using the raw spectra normalized by absorbance at 1654 nm gave the best prediction. The waveband at 1654 nm was associated with C–H stretch first overtone which may be related to aromatic compounds in the peel. The model predicted TA with *SEP* of 0.076% which was significantly lower than that predicted by the raw spectra model (*SEP*=0.097%). This was a significant improvement in prediction of TA in intact tangerine. However the *RPD* (standard deviation of reference data of the prediction sample set divided by *SEP*) was relatively low (*RPD*=1.7). Further work is necessary to improve the predictability of TA in intact tangerines by NIR spectroscopy.

Conclusion

PLS-DA was conducted to determine the peel spectral information which separated a group of intact tangerines from that of peeled tangerines. Absorbances at wavelengths associated with high values of x-loading weights of the first PC were used to normalize and center the raw spectra prior to building the new models. Significant improvement in TA prediction was found using the model built on the raw spectra normalized by the absorbance at 1654 nm.

Acknowledgements

The authors would like to thank Kasetsart University Research and Development Institute (KURDI) for the research financial support and Kasetsart Agricultural and Agro-Industrial Product Improvement Institute (KAPI) for instrument and technical supports.

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