

Full Paper

Application of FT-NIR spectroscopy to the measurement of fruit firmness of “Fuji” apples

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Abstract: This paper indicates the possibility of using near infrared (NIR) spectroscopy as a rapid method of predicting quantitatively fruit firmness of apple. A hundred “Fuji” apples were used as the study target in the experiment. A partial least square (PLS) algorithm was used to perform the calibration. To decide upon the number of PLS factors included in the PLS model, the model was chosen according to the lowest root mean square error of cross-validation (RMSECV) in training. The correlation coefficient R between the NIR predicted and the reference results for the test set were used as an evaluation parameter for the models. The best experimental results were obtained as follows: the PLS calibration model in fruit firmness determination was achieved with 12 PLS factors under MSC preprocessing method. The correlation coefficient between the NIR spectroscopy prediction results and reference measurement result was $R = 0.74893$. The study demonstrates that NIR spectroscopy technology with multivariate calibration analysis could be successfully applied as a rapid method to predict fruit firmness of apples.

Keywords: FT-NIR spectroscopy, apple, fruit firmness, PLS, RMSECV

Introduction

Apples are one of the most popular fruits across the world. “Fuji” apples are one of the most cultivated commercial apple cultivars in global production. With a raised consumption, quality control

of apples is becoming increasingly important. Fruit firmness is one of the important quality parameters used for assessing apple quality [1-6]. Currently, fruit firmness is commonly measured with the Magness–Taylor (MT) firmness tester or similar testing devices. Yet, this quality measurement method is often destructive, inefficient or time consuming, and prone to operational error. Thus, a nondestructive sensing technique that is capable of measuring quality parameters of apple including fruit firmness would be of great value in ensuring consistently high quality fruits for the consumer.

Abundant literature exists on nondestructive sensing techniques for determining fruit firmness. For example, multispectral imaging based on light scattering principle was attempted to measure the internal quality of fruits including firmness [7-10]. First, the absorption and scattering properties of apple tissue over the visible and near infrared regions were acquired by multispectral imaging system, then a curve fitting algorithm for a steady-state diffusion theory model was proposed to determine absorption and reduced scattering coefficients from the spatially-resolved multispectral reflectance profiles. Finally, predictive model for measuring apple fruit firmness and soluble solid content (SSC) were calibrated by simple multi-regression analysis. Although, multispectral imaging is simple, fast and easily applied to measuring fruit firmness, precision of measuring results is not satisfying, especially in measuring fruit firmness; the correlative coefficient is often less than 0.7.

Additionally, in measuring fruit firmness, past research was largely focused on using mechanical methods, such as quasi-static compression, vibration, impact, and sonic or ultrasonic sensing [11-13]. These mechanical techniques have shown potential for measuring fruit firmness, but they are often difficult to implement or too slow for online sorting application. Therefore, it is necessary to replace time-consuming methods with a fast, accurate and nondestructive technique.

Near-infrared (NIR) spectroscopy has been proven to be a powerful analytical tool used in the agricultural, nutritional, petrochemical, textile and pharmaceutical industries [14-22]. It is a fast, accurate and non-destructive technique that can be used as a replacement of time-consuming chemical method. Near-infrared (NIR) spectroscopy has also proven to be effective for quantitatively analysing internal quality of fruits. Many studies on measuring fruit firmness of apple with NIR spectroscopy were cited [23-24].

In order to apply FT-NIR to predict quantitatively fruit firmness of apple, it is necessary to build a reliable calibration model. The objective of this research is to develop and prove the applicability of multivariate calibration to NIR data. The different steps that have to be undertaken in multivariate calibration were systematically studied. The partial least square (PLS) model was used and the study focused on the effect of the number of PLS factors and the method of spectral preprocessing. The robustness of the final PLS model was evaluated according to the root mean square error of cross-validation (RMSECV), the root mean square error of prediction (RMSEP), and the correlation coefficient (R).

Materials and Methods

Apple fruit samples

For this research, 100 “Fuji” apples were purchased from the local market in Zhenjiang City, Jiangsu Province of China. All of the apples were sent to the laboratory and non-destructively analysed

by diffuse reflectance FT-NIR spectroscopy between 10,000-4,000 cm^{-1} , and also destructively analysed by a texture analyser for fruit firmness.

The apples were divided into two groups. The first group consisted of 60 apples used for developing the calibration model. The second group consisted of 40 apples used for prediction models. Each apple was measured at four equally spaced positions along the equator. For the reference measurement using a texture analyser, the measurement was conducted on peeled apples.

Spectral data acquisition

The reflectance NIR spectra of intact apples were measured by a FT-NIR spectrometer (AntarisTM II analyser, Thermo Electron Corporation, USA) with integrating sphere sampling module. The FT-NIR spectrometer had a spectral range of 10,000-4,000 cm^{-1} (1,000-2,500 nm) and the resolution was set at 8.0 cm^{-1} with 3.856 cm^{-1} data intervals, each spectrum having thus 1,557 data points. The number of the spectral scans was 32 in this experiment.

Figure 1 shows a schematic diagram of NIR diffuse reflectance measurement set-up. Diffuse reflectance measurement is simplified by using an integrating sphere. The light beam is directed into the sphere and travels directly through the center of the sphere and the optical window into the apple sample. The beam scatters off the sample and the reflected light beams re-enter the sphere. The inside of the sphere is coated with diffuse gold, which collects the light beams and directs them to the detector [25].

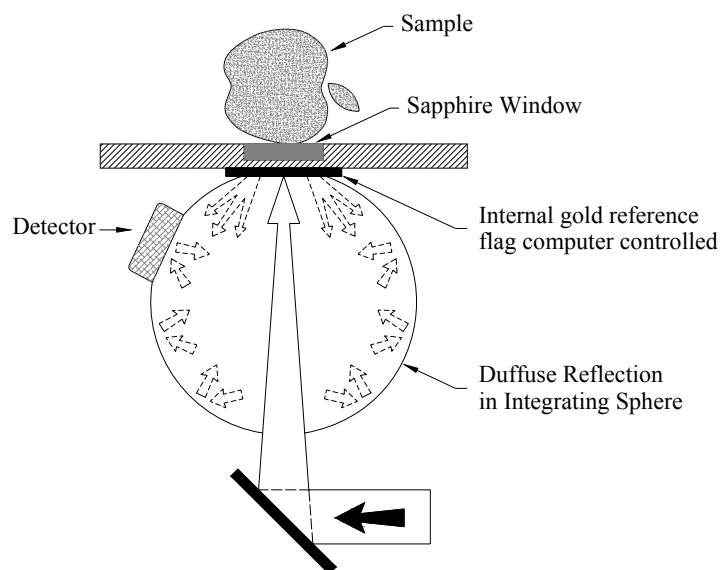


Figure 1. Schematic diagram of NIR diffuse reflectance measurement set-up

Each spectrum was recorded as $\log(1/R)$ where R was fractional reflectance, by averaging 32 scans of spectra. Four reflectance spectra were measured at 4 positions on each apple around the equator. After that the four reflectance spectra were averaged to provide a mean spectrum for calibration and validation set.

The original reflectance spectral data of 100 apple samples is shown in Figure 2. Partial least square (PLS) algorithm of multivariate calibration was attempted several times to determine the optimal spectral range for building calibration model. It was found that the optimal spectral range of fruit firmness of apples was $9,391\text{-}6,886\text{ cm}^{-1}$.

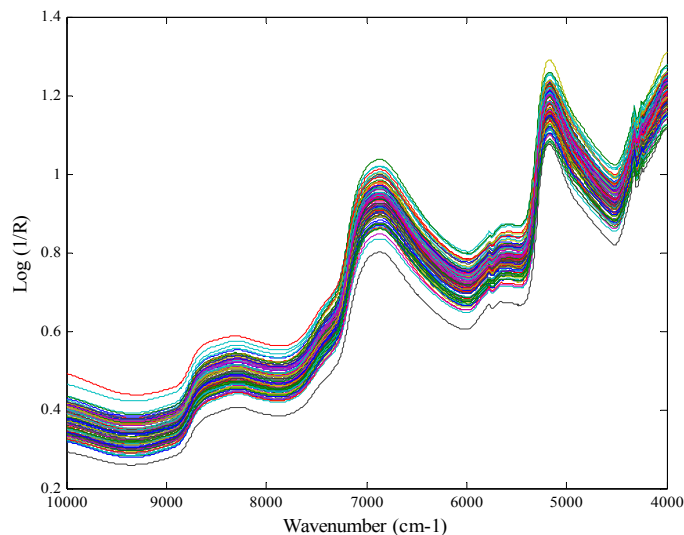


Figure 2. Original reflectance spectra as log (1/R) for 100 apple samples

Reference measurements

The destructive measurement on the apples in this research was conducted to determine the fruit firmness. It was measured with a texture analyser (Model TA-XT2i, Stable Microsystem, Ltd., England). This measurement was carried out exclusively on peeled apples, thus applying only to apple flesh. Fruit firmness parameters in this experiment included 1.0 mm/s test speed, 10.0 mm penetration distance and 100 g force setting with 3-mm diameter stainless cylinder probe. Maximum flesh rupture force was analysed in this research.

The measuring procedure was similar to that for FT-NIR. Each apple was measured at the same four positions around the equator. The mean value of firmness was the average of 4 measurements for the calibration and validation sets.

Spectral preprocessing methods

In this study, the spectral data were analysed using PLS regression with preprocessing. Four spectral preprocessing methods were applied comparatively; these were standard normal variate (SNV), mean centering, multiplicative scatter correction (MSC) and min/max normalisation method, respectively. First, SNV, a mathematical transformation method of the spectra, was used to remove slope variation and to correct for scatter effects. Each spectrum was corrected individually by first centering the spectral values, then the centred spectrum was scaled by the standard deviation calculated from the individual spectral values. Second, mean centering method process was used to calculate the average spectrum of the data set and subtract that average from each spectrum. Third,

MSC was used for the correction of scattered light on the basis of different particle sizes. The technique was used to correct for additive and multiplicative effects in the spectra. Finally, min/max normalisation, a type of normalisation, was utilised to transform the data into a desired range by subtracting the minimum value of an attribute from each value of the attribute and then dividing the difference by the range of the attribute [26]. Generally, the range of the spectral value after min/max normalization spectral preprocessing is set [0 1]. Figure 3 shows the results of different methods after preprocessing.

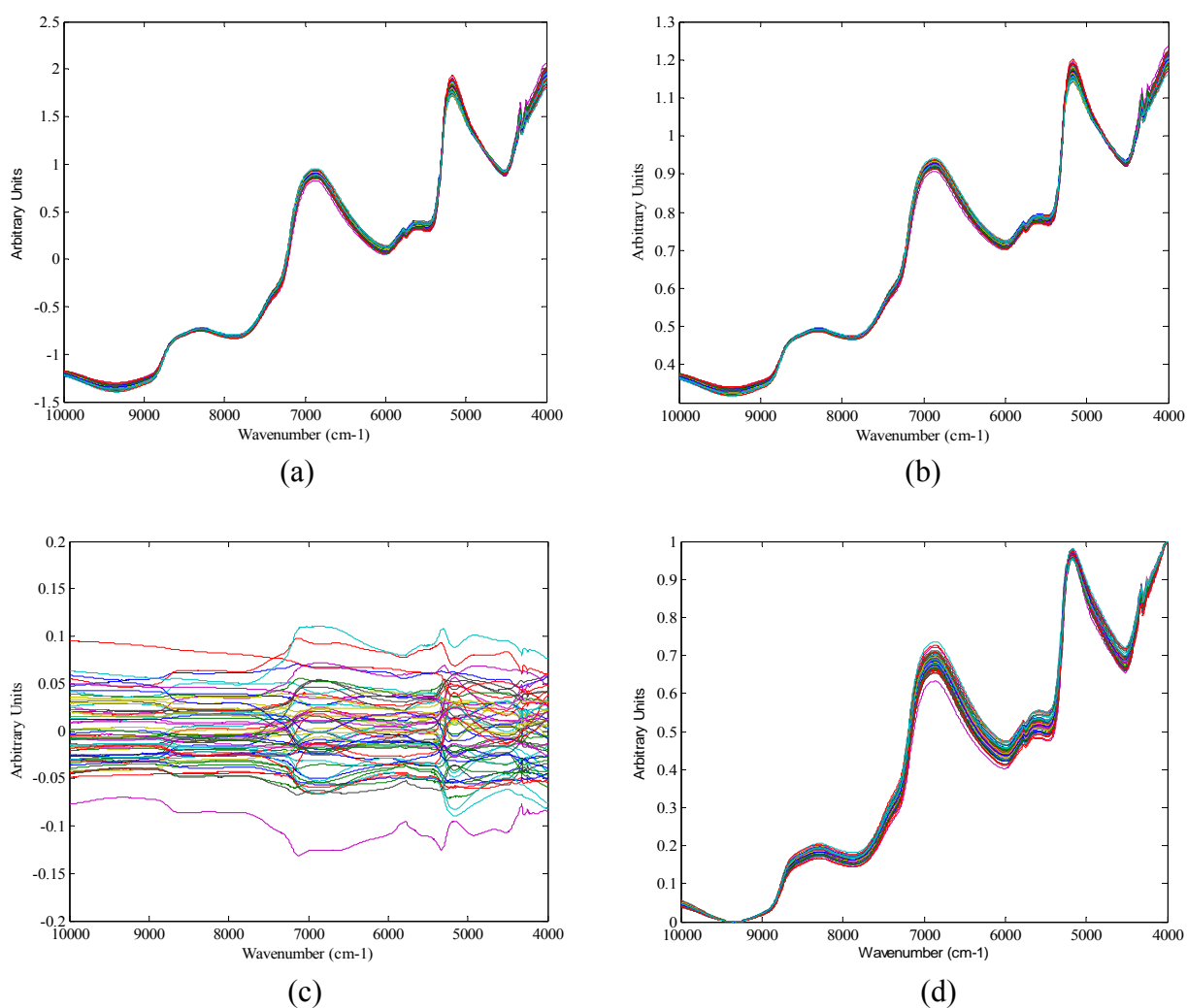


Figure 3. Preprocessed reflectance spectra of apple: (a) SNV (b) MSC (c) mean centering (d) min/max normalisation

Software

All methods were performed in Matlab V.7.1 (Mathworks, Natick, USA) for Windows XP. For the spectral acquisition, Result Integrating Program (Thermo Electron Result Integration and Result Operation Software, Thermo Electron Corporation, USA) was used.

Results and Discussion

Quantitative analysis of the PLS models

One hundred “Fuji” apple samples were selected to build the PLS model in this experiment. All 100 spectra were divided into a training set and a test set. To avoid bias in subset selection, this division was arranged as follows: all samples were sorted according to their respective y-value (viz. the reference measurement value of fruit firmness). In order to come to a 3/2 division of training/test spectra, three spectra from every five samples were selected for the training set, and two spectra from every five samples were selected for the test set, so that finally the training set contained 60 spectra (see Table 1) and the remaining 40 spectra constituted the test set (see Table 2). As seen in Tables 1 and 2, the range of y values in the training set covers the range in the test set, therefore the distribution of the samples was appropriate in training and test sets.

Table 1. Reference measurement and sample number in training set

Component	Unit	S.N.	Range	Mean	S.D.
Fruit Firmness	gf	60	133.28-817.00	446.77	148.91

(S.N., sample number; S.D., standard deviation; gf, gram force unit)

Table 2. Reference measurement and sample number in test set

Component	Unit	S.N.	Range	Mean	S.D.
Fruit Firmness	gf	40	151.45-811.02	446.39	149.37

(S.N., sample number; S.D., standard deviation; gf, gram force unit)

The performance of the final PLS model was evaluated in terms root mean square error of cross-validation (RMSECV), the root mean square error of prediction (RMSEP), and the correlation coefficient (R). For RMSECV, a leave-one-sample out cross-validation was performed: the spectrum of one sample of the training set was deleted from this set and a PLS model was built with the remaining spectra of the training set. The left-out sample was predicted with this model and the procedure was repeated by leaving out each of the samples of the training set. RMSECV was calculated by Eq.1 as shown:

$$RMSECV = \sqrt{\frac{\sum_{i=1}^n \left(\hat{y}_i - y_i \right)^2}{n}} \quad (1)$$

where n was the number of samples in the training set, y_i was the reference measurement result for sample i, and \hat{y}_i was the estimated result for sample i when the model was constructed with sample i removed. The number of PLS factors included in the model was chosen according to the lowest

RMSECV. This procedure was repeated for each of the preprocessed spectra. For the test set, the root mean square error of prediction (RMSEP) was calculated by Eq. 2 as follows:

$$RMSEP = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n}} \quad (2)$$

where n was the number of apple samples in the test set, y_i was the reference measurement result for test set sample i , and \hat{y}_i was the estimated result of the model for test sample i . Finally, the model with the overall lowest RMSECV was selected as the final model. Correlation coefficients between the predicted and the measured value were calculated for both the training and the test set, which were calculated as follows (Eq. 3):

$$R = \sqrt{1 - \frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}} \quad (3)$$

Fruit firmness

The model with the overall lowest RMSECV was selected as the final model. Figure 4 shows RMSECV plots as a function of PLS factors for determining fruit firmness by different spectral preprocessing methods. The RMSECV values decreased sharply with increasing numbers of PLS factors, which are shown in Figure 4. The optimal PLS numbers of SNV, MSC, mean centering and min/max normalisation spectral preprocessing methods were equal to 12, 12, 14 and 12, respectively.

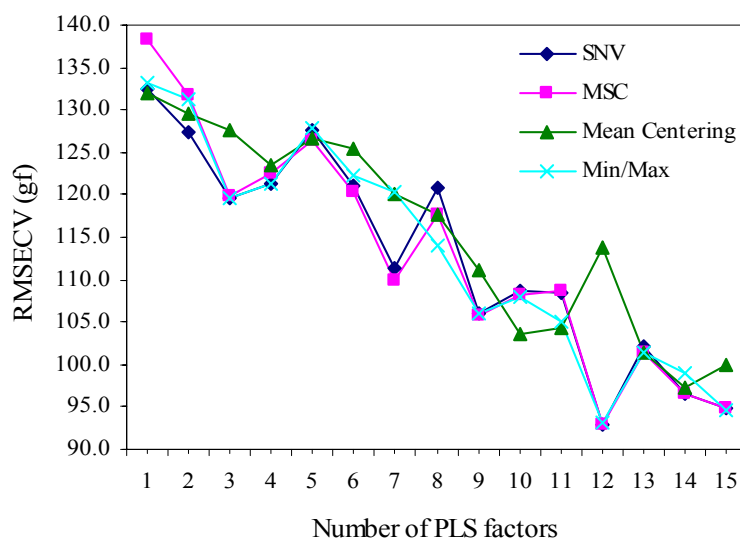


Figure 4. Effect of number of PLS factors on RMSECV for fruit firmness calibration model

Table 3 shows the best results of the models by different spectral preprocessing methods for determining the prediction of the fruit firmness. As seen in Table 3, the difference of RMSECV was slight for SNV, MSC and min/max normalisation spectral preprocessing methods. The optimal PLS number of these three spectral preprocessing methods was equal to 12, while that of the mean centering spectral preprocessing method was equal to 14. However, in this application MSC spectral

Table 3. Best results for each of the processing methods for the models of fruit firmness

Preprocessing method	PLS factors	RMSECV (gf)	RMSEP (gf)	R (train)	R (test)
SNV	12	92.930	99.371	0.69682	0.74661
MSC	12	92.910	98.980	0.69698	0.74893
Mean centering	14	97.254	100.890	0.66074	0.73741
Min/max normalization	12	93.173	95.409	0.69489	0.76942

(gf = gram force unit)

preprocessing method was optimal and selected to build the calibration model, due to its lowest RMSECV value. Therefore, the best predictive model was achieved with 12 PLS factors after MSC spectral preprocessing method, in which the values of RMSECV and RMSEP were 92.910 gf and 98.980 gf, respectively. The correlation coefficients for training and test set were 0.69698 and 0.74893, respectively, and Figure 5 shows the scatter plots of the model for determining fruit firmness by MSC spectral preprocessing method, which was selected in this study.

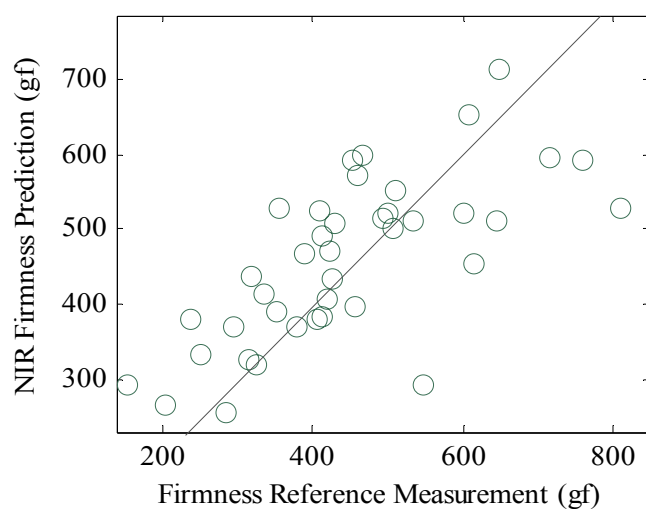


Figure 5. Reference determination versus NIR prediction for fruit firmness of training set data

Conclusion

The overall results in this research sufficiently indicate that it is possible to use this non-destructive technique for measuring fruit firmness in “Fuji” apples and that fruit firmness can be determined by FT-NIR spectroscopy using the spectral range of 10,000-4,000 cm^{-1} . The PLS method has the potential to estimate the calibration and prediction model from their near infrared spectra. The PLS calibration model in fruit firmness determination was achieved with 12 PLS factors under MSC preprocessing method. The correlation coefficient between the NIR spectroscopy prediction results and reference measurement results was $R = 0.74893$. It could be concluded that the fruit firmness of apple could be analysed quickly and simultaneously by NIR spectroscopy coupled with the appropriate chemometric methods, and this real-time, on-site measurement would significantly improve the efficiency of quality control and assurance.

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