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Measurement of sugar content in Fuji apples by FT-NIR spectroscopy*

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Abstract: To evaluate the potential of FT-NIR spectroscopy and the influence of the distance between the light source/detection probe and the fruit for measuring the sugar content (SC) of Fuji apples, diffuse reflectance spectra were measured in the spectral range from 12500 to 4000 cm^{-1} at 0 mm, 2 mm, 4 mm and 6 mm distances. Four calibration models at four distances were established between diffused reflectance spectra and sugar content by partial least squares (PLS) analysis. The correlation coefficients (R) of calibrations ranged from 0.982 to 0.997 with SEC values from 0.138 to 0.453 and the SECV values from 0.74 to 1.58. The best model of original spectra at 0 mm distance yielded high correlation determination of 0.918, a SEC of 0.092, and a SEP of 0.773. The results showed that different light/detection probe-fruit distances influence the apple reflective spectra and SC predictions.

Key words: FT-NIR spectroscopy, Nondestructive measurement, Sugar content, Fuji apples, Partial least squares analysis
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INTRODUCTION

Recently increasing demands from consumers have been observed for premium quality fruit with better taste at a higher price. Three major parameters determine the internal quality and the taste of apples. These are hardness, sugar content and titratable acidity, which are still determined destructively. Near-infrared spectroscopy (NIRS) has been used to nondestructively measure internal quality in a wide range of fruits and vegetables, such as onions (Birth *et al.*, 1985), cantaloupe (Dull *et al.*, 1989), melons (Dull *et al.*, 1992), mandarin (Kawano *et al.*, 1993), peach (Kawano *et al.*, 1992; Kawano and Abe, 1995), nectarines (Slaughter, 1995), apple (Moons *et al.*, 1997; Lammertyn *et al.*, 1998; Peirs *et al.*, 1999; 2001; Lu and Ariana, 2002; McGlone *et al.*, 2002) and kiwifruit (Jordan *et al.*, 1997).

Recent advances in Fourier transform NIR (FT-NIR) spectroscopic instrumentation and multivariate data analysis techniques have had significant impact on the determination of food composition. FT-NIR improves spectra reproducibility and wavenumber precision which can minimize the effects of solvent interference.

The objectives of this study were (1) to evaluate FT-NIR spectrometry for measuring the sugar content of Fuji apples and to establish relationships between the nondestructive FT-NIR spectral measurements and sugar content of apple fruit; (2) to quantify the influence of four distances between the light source/detection probe and the fruit on the

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apple spectral measurement and sugar content prediction.

MATERIALS AND METHODS

FT-NIR measurements

Diffuse reflectance in the 12500 to 4000 cm^{-1} region were measured for 22 apples from distance of 0 mm, 2 mm, 4 mm and 6 mm.

Our equipment (Fig.1) consisted of a wide band light source (50 W quartz halogen, Nicolet, USA), a bifurcated optical configuration (Type 847-072200) and a fruit holder/light collection fixture. Intact apples were placed on the fruit holder, with the stem-calyx axis horizontal. In the head of the bifurcated cable, the source and detector fibers (NA: 0.22 and 250 um core diameter) were arranged randomly (Fig.1). Light was guided to the sample by source fibers, and the light backscattered from the sample was received by the detector fibers and delivered to Nexus FT-NIR spectrometer with spectral range of 12500 cm^{-1}–4000 cm^{-1} at 2.0 cm^{-1} sampling interval; and the interferograms (64) were co-added followed by strong Beer-Norton apodization. The total number of data points was 3001 for each spectrum. A high-speed ADC electronics unit was used to amplify and digitize the spectral signal. To avoid surface reflectance and ensure subsurface penetration of the light into the apple flesh, the bifurcated optical probe was placed at 75° to horizontal. Eleven mm diameter rubber grommet with different thickness (2 mm, 4 mm and 6 mm) acted as a flexible support to accommodate different shaped apples. All spectra were first converted to relative reflectance by dividing each sample spectrum by a standard reference spectrum. The standard reference spectrum, obtained by placing a 22 mm diameter, 19 mm high cylindrical Teflon block directly above the fruit holder, was measured after every ten fruit during the experiments.

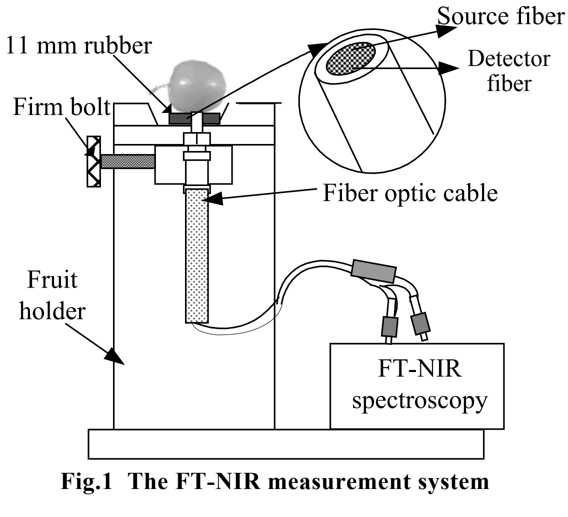

Fig.1 The FT-NIR measurement system

Each spectrum was recorded as log (1/*R*), where *R*=relative reflectance, by averaging 32 scans. Four separate spectral measurements were made on each apple with the locations 90° apart around the equator of the fruit, avoiding any obvious surface defects (bruises, scars, etc.). Four relative reflectance spectra were averaged to provide a mean spectrum for each apple.

To obtain enough sensitivity in measuring the diffuse reflectance of the intact fruit, the experiment setup of FT-NIR spectroscopy was as follows (Table 1).

Table 1 The experiment setup of FT-NIR

Preferences	Value
Spectral range (cm^{-1})	12500–4000
Sampling interval (cm^{-1})	2.0
Scan number (n/s)	32
Resolution (cm^{-1})	4.0
Mirror velocity (cm/s)	0.9494
Aperture size	20

Measurement of sugar content

Sixty Fuji apples used for the experiment were purchased at a supermarket and stored for 2 days at 19 °C and 68% relative humidity. Sugar content measurement was made with a hand-held sugar-refractometer (WYT-4, Quanzhou Optical Instruments Company). The mean value of the sugar content for each apple was the average of four measurements that were made by extracting juice from the four positions of the spectra acquisition.

Data analysis and modeling

Fig.2 shows typical relative reflectance spectra of highest and lowest SC in the range of 12500 cm^{-1} to 4000 cm^{-1}, since the spectral data below

Table 2 Statistical data on sugar content in apple

Types	Number	Range	Mean	S.D.	CV%
Sugar content in calibration	46	7.7	13.28	2.32	17.49
Sugar content in prediction	14	6.0	13.09	1.96	14.94

11000 cm^{-1} and above 4400 cm^{-1} contained considerable noise, the wavelengths of 11000 cm^{-1} to 4400 cm^{-1} were used in this study.

The relative reflectance curves were smoothed using the Savitsky-Golay method at a gap of 25 data spectra. Once these preprocessing procedures were completed, partial least squares method (PLS) was used to develop calibration models for predicting the sugar content. About 75% of the sample fruit were randomly selected for calibration and the remainder were used for evaluating the model prediction error. The calibration (SEC) and standard error of cross-validation (SECV), were used to measure the model's performance. The *SEC* and *SECV* are calculated as follows:

$$SEC=\sqrt{\frac{\sum_{i=1}^{n}(y_{\mathrm{c}}-y_i)^2}{n-1}} \quad (1)$$

$$SECV=\sqrt{\frac{\sum_{i=1}^{N}(y_i-y_{\mathrm{p}})^2}{N}} \quad (2)$$

Where y_i is ^{0}Brix by refractometer, y_{c} is the NIR calibrated value, y_{p} is the NIR predicted value, n is the number of samples used in calibration and N is the number of samples used in prediction.

RESULTS AND DISSCUSSION

Comparison of PLS calibrations at four distances

By PLS analysis of TQ Analyst v6.0 (Nicolet company), the selected wavenumbers used to develop the calibration equation were about 11000–4400 cm^{-1}. Considering the small samples of 22, we adapted the modification of the classical PLS algorithm that involved the standardization of the residuals after each iteration. Hence, the calibration routine yielded automatically cross validations and one sample was taken out each time when performing PLS. The results of PLS models at different distances are presented in Table 3.

From Table 3, the highest correlation of calibration was the model at 2 mm distance with a high coefficient of correlation (0.997), the second was at 6 mm distance and the lowest correlation was at 4 mm distance.

The prediction performance of the different calibration models for four distances by PLS analysis is presented in Table 4. As only 22 samples

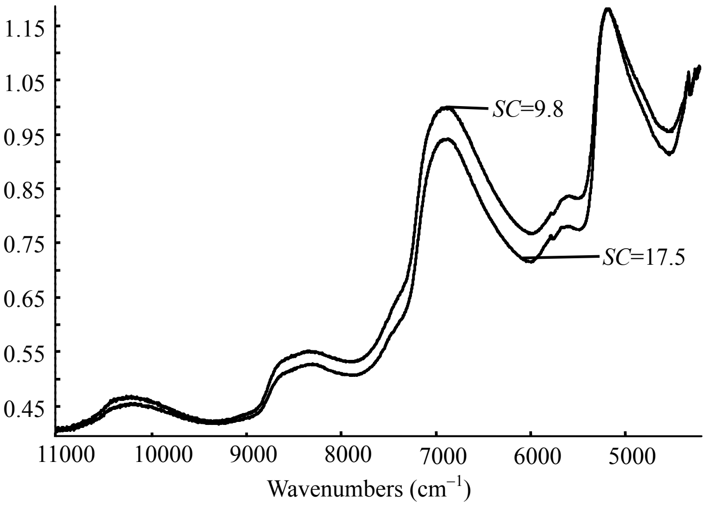

Fig.2 FT-NIR spectra of intact Fuji apples with the highest and lowest ^{0}Brix

Table 3 The relationship between the Lab SC(%) and FT-NIR SC(%) at different distances

Distances	*N*	Equation	*Corr.*
0 mm	22	y=0.9886x+0.1494	0.982
2 mm	22	y=0.9985x+0.0203	0.997
4 mm	22	y=0.7775x+3.0155	0.977
6 mm	22	y=0.9461x+0.7078	0.989

Note: *N*: sample size; *Corr.*: correlation coefficient; *y*: FT-NIR predicted SC(%); *x*: Lab measured SC(%)

Table 4 The prediction performance of the different calibration at different distances

Distances	No. of factor	*SEC*	*SECV*	R^2
0 mm	5	0.402	0.74	0.94
2 mm	5	0.138	1.15	0.85
4 mm	4	0.453	1.58	0.66
6 mm	4	0.313	1.37	0.79

were used for this experiment, we used cross-validation method and one sample was taken out from the calibration set when performing PLS. The standard error of cross-validation (SECV) is given in Table 4 and the influence of the number of factors on the prediction residual error sum of square (PRESS) is shown in Fig.3.

Tables 3 and 4 show that the calibration model at 0 mm distance had high correlation determination of 0.94, a low SEC of 0.402, low SECV of 0.740 and a small difference between SEC and SECV and so further experiment on predicting the sugar content of apple by FT-NIR spectroscopy was based on it.

Fig.3 shows that PRESS increased with increasing distances and that only 4 or 5 factors were used in the calibration model.

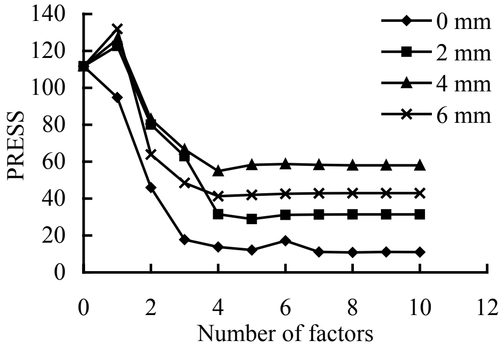

Fig.3 The influence of number of factors on the prediction

Calibration and prediction analysis at 0 mm distance

Sixty samples were used for this experiment and 46 samples were used to develop the calibration model.

In Fig.4 and Fig.5, the data from the final SC calibration process are shown plotted against measurement values for the 60 fruit set. The correlation coefficient was 0.999; the standard error of calibration (SEC) of the calibration fruit was 0.092; and the standard error of prediction (SEP) was 0.773.

One sample was taken out each time when performing PLS. The correlation determination (R^2) was 0.879 and the SECV was 0.811.

Discussion

It is essential that the fruit of the prediction dataset have the large different distribution as those of the calibration data set. In our experiment, there was some different distribution between calibration

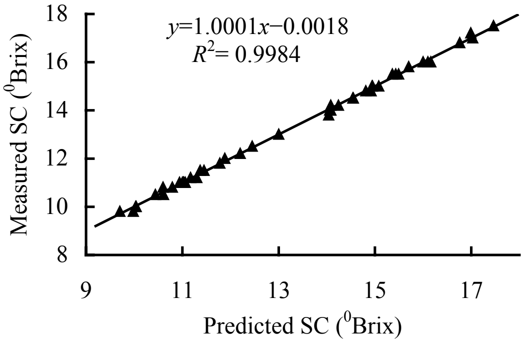

Fig.4 Scatter plots of measured versus predicted for calibration model

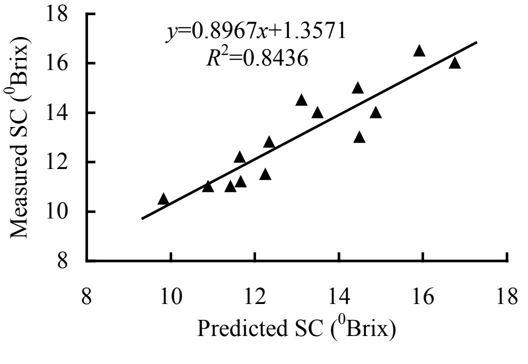

Fig.5 Scatter plots of measured versus predicted SC for prediction model

and prediction data set (Table 2) because of the limited sample size. Another limit was the inherent variation of the ^{0}Brix value in individual fruits, which showed a relatively high SEP (0.773), although we adapted the cross validation method to estimate the calibration and validation errors and the SECV was 0.811. The main reasons for this result may include: (1) The sample sizes were too small and induced a narrow range of constituent values; (2) The signal-to-noise ratio could be improved in this experiment by increasing the scan number (Table 1).

CONCLUSIONS

This research indicated that it is possible to develop a nondestructive technique for measuring Fuji apple sugar content by FT-NIR spectroscopy. PLS calibration technique was used for establishing four calibration models of the relation between diffused reflectance spectra and sugar content at four distances. The correlation coefficients (*R*) of calibrations ranged from 0.982 to 0.997, SEC values from 0.138 to 0.453 and SECV values from 0.74 to 1.58. The best model of original spectra at 0 mm distance yielded a high correlation determination of 0.918, SEC of 0.092, and a relatively high SEP of 0.773.

The results showed that different light/detection probe-fruit distances influence the apple reflective spectra-and SC predictions. This influence should be considered in the apple spectral measurement.

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