Development of robust calibration for determining apple sweetness by near infrared spectroscopy

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Introduction

Sweetness is a main quality factor contributing to the fruit taste. Most consumers require tasty and fresh fruit at a reasonable price. Near infrared (NIR) spectroscopy has been used successfully to estimate sweetness of various fruits[1–3] non-destructively, allowing the sweetness grading of individual fruit. In previous studies we expressed the sweetness as a Brix (by refractometer), total or individual sugar content (by HPLC analysis) and sweetness score (by calculating the sweetness index), comparing the calibration accuracy of each expression method.[4,5] Calibration samples for these models involved only one cultivar, one growing district and one harvest year. According to previous reports, some factors, such as harvest year, variety and growing season, affect the calibration model for sweetness of fruit. Peiris *et al*.[6] reported on the calibration of NIR spectra with the soluble solid of peaches which were collected over three years. Guthrie *et al*.[7] reported on the robust calibration for pineapple Brix across growing seasons and Miyamoto *et al*.[8] investigated the influence of various factors on a calibration model for mandarin Brix.

In this study, we investigated the influence of two variables, growing district and harvest year, for calibration and developed a robust model for the determination of sweetness of F*uji* apple fruit.

Materials and methods

Apple fruits

About 2000–3000 apple fruits (*Fuji*) from 1995 to 1999 were collected from Andong, Youngchun and Chungsong in Korea and used in calibration and prediction.

Chemical analysis

After the NIR spectra were collected, part of the sample was squeezed and the Brix value was measured with an Atago (Japan) digital refractometer.

NIR spectra

NIR spectroscopic analyses were performed using an InfraAlyzer 500C (Bran+Luebbe, Germany) and the instrument was operated by the software package IDAS. For spectra collection a sample holder[9] was used. The reference spectral data were scanned over the range of 1100 to 2500 nm at 2 nm intervals to give701 data points and stored as log (1/*R*). A polystylene was used as background material. The temperature of the fruit was maintained at 15°C.

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Table 1. Modelling of sample sets and range of reference Brix values.

Model	Growing district	Harvest year	Brix		
			Minimum	Maximum	Mean
Model 1	Andong	1995	12.5	17.6	14.8
Model 2	Youngchun	1995	10.9	16.9	14.3
Model 3	Chungsong	1995	11.4	15.9	13.8
Model 4	Andong	1996	13.5	16.6	15.0
Model 5	Andong	1997	12.5	15.7	14.6

Data analysis

Spectral data were imported into Sesame software, version 3.0 and reference values inputted. Samples were assigned to calibraiton and prediction sets according to Brix value. Two samples with maximum and minimum value were located to the calibration set and the other samples were allocated to the calibration set and prediction set in the ratio of 3 to 2, respectively. The data analysis was performed by stepwise multiple linear regression (MLR) using raw spectra data with no pre-processing. Calibration statistics included the correlation of coefficient (*R*), standard error of prediction (*SEP*) and bias.

Results and discussion

Characteristics of apple Brix

Table 1 shows modelling for the calibration set and Brix value of each sample set. Brix value varies from 10.9 to 17.6 and each sample set has a different range of Brix value. The Chungsong sample set has a relatively narrow range, (11.4 to 15.9) and low mean value of Brix compared with the Andong and Youngchun sample sets. The Andong samples showed higher Brix value than the other district's samples. Each model has different variables such as growing districts and harvest years, respectively.

Influence of growing districts

Table 2 shows the calibration and prediction results of models 1, 2 and 3. Correlation coefficients (*R*) of the models were over 0.95 with the exception of model 2. Each calibration model was successfully predicted to its own sample set. *SEP* were 0.47 for Andong, 0.85 for Youngchun and 0.80 for

Table 2. The results of MLR calibration and prediction for models 1, 2 and 3 of Table 1.

Calibration		Prediction					
Model	*R*	Andong		Youngchun		Chungsong	
		SEP	Bias	*SEP*	Bias	*SEP*	Bias
Model 1	0.96	0.47	0.044	1.32	–0.304	1.05	–0.487
Model 2	0.85	1.32	–0.447	0.85	0.280	1.83	1.303
Model 3	0.95	1.64	–1.430	1.16	–0.240	0.80	0.448

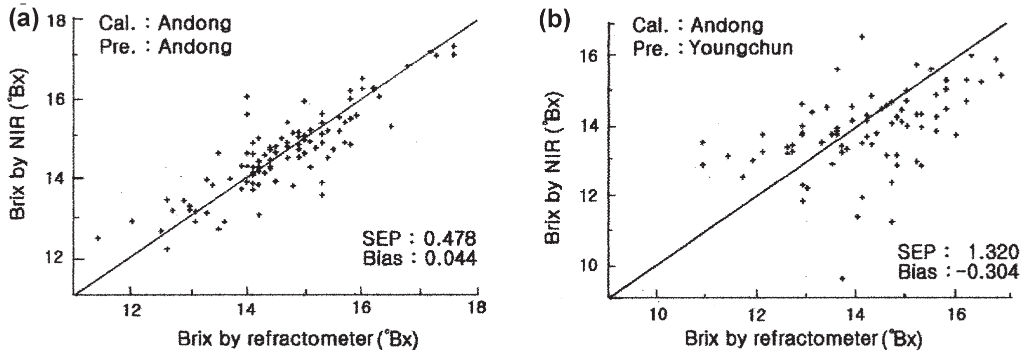

Figure 1. NIR *vs* actual Brix value of the apple fruit, representing the prediction results of (a) the Andong sample set and (b) the Youngchun sample set with the Andong calibration model.

Table 3. Prediction result of each sample set with the combined calibration model for growing districts.

Calibration		Prediction							
Model	*R*	Andong		Youngchun		Chungsong		Combined	
		SEP	Bias	*SEP*	Bias	*SEP*	Bias	*SEP*	Bias
Combined	0.94	0.78	–0.290	0.81	0.060	0.58	0.121	0.69	–0.075

Chungsong, respectively. However, each model was poorly predicted to the other sample sets, indicating a higher *SEP* and a higher bias. For example, the Youngchun and Chungsong sample sets were predicted poorly to the Andong calibration (model 1) with higher *SEP* and bias. As shown in Figure 1(b), there is an unaccesptable scatter relationship between NIR analysis and the reference method.The same results were obtained when the Younchun samples were predicted to models 1 and 3 and the Chungsong samples were predicted to models 2 and 3. These results indicate that the calibration model developed using one district's samples could not be used with the samples grown in other districts.

Table 3 shows the calibration statistics of the combination sample set which combined three sample sets, models 1, 2 and 3. This model resulted in an acceptable error level. *SEP* were 0.78 for Andong, 0.58 for Younchun and 0.69 for Chungsong samples, respectively.

Figure 2 shows the scatter plot of NIR predicted vs reference Brix of apple using the combined calibration model.

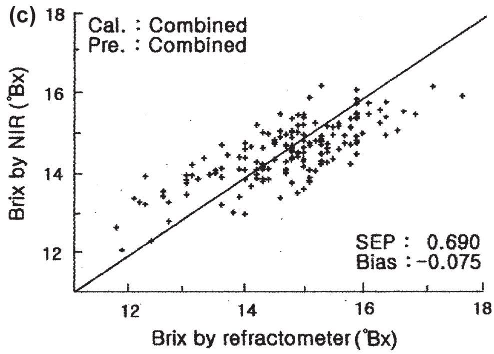

Figure 2. NIR *vs* actual Brix of apple fruit, showing the prediction result of thecombined prediction sets with the combined calibration models for growing the districts.

Influence of harvest year

Table 4 shows the calibration and prediction results of models 1, 4 and 5. The correlation coef-

Table 4. Calibration and prediction results of MLR models 1, 4 and 5 of Table 1.

Calibration	Prediction						
Model	*R*	1995		1996		1997	
		SEP	Bias	*SEP*	Bias	*SEP*	Bias
Model 1	0.96	0.47	0.044	4.75	–4.640	2.40	–2.250
Model 4	0.94	1.13	0.945	0.51	0.075	1.67	1.546
Model 5	0.91	0.79	–0.023	3.90	–3.827	0.41	0.001

ficients (*R*) of the three models were all over 0.9. Each calibration model predicted its own sample set successfully, as shown in Figure 3(a). The *SEP* was 0.47 for 1995, 0.51 for 1996 and 0.41 for 1997, respectively. But each model could not predict to the other sample sets successfully. When the 1997 samples predicted to the 1995 model, high *SEP* and bias were obtained (2.40 and –2.25, respectively), as shown in Figure 3(b). The scatter plots show a big bias effect. This indicates that the calibration model developed using samples having a limited growing year could be predicted to its own sample set well but could not be predicted to the samples grown in other years.

Table 5 shows the result of each sample set predicted with the combined model for the harvest year. The combined model was developed using a combination sample set of 1995, 1996 and 1997. Prediction resulted in SEP of 0.53 and 0.58 for 1995 and 1997 samples, respectively. This is less accurate than those by their own calibration models. However, the 1996 set showed better results. The *SEP* decreased to 0.47. Figure 4 shows the scatter plot for the reference sweetness vs predicted values from the NIR spectra using the above comination model. The *SEP* was 0.53 and bias was 0.004. These results indicate that the combined model could be used for determining sweetness of apples harvested for each year with acceptable accuracy.

Consequently, when the calibration sample has a sufficient variable range for different origins such as growing district and harvest year, it is possible to develop a robust calibration equation.

Climate and soil conditions could affect fruit sweetness. The best prediction results can be obtained when the calibration set and prediction set have the same conditions. However, it is impossible

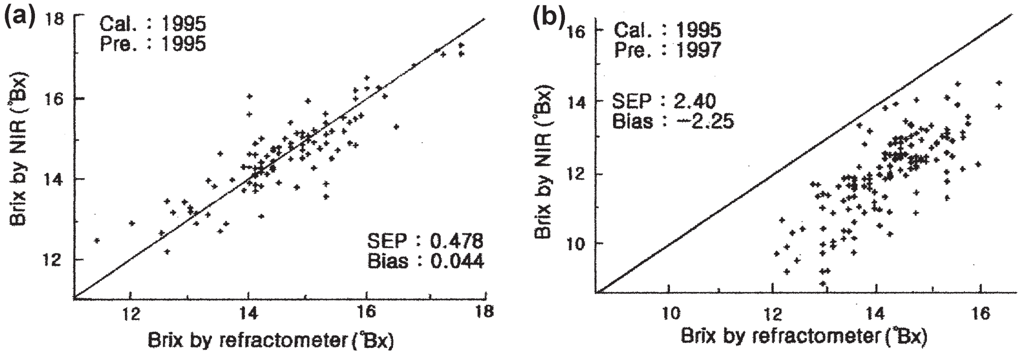

Figure 3. NIR *vs* actual Brix of apple fruit, representing the prediction results of the (a) 1995 sample set and (b) 1997 sample set with the 1995 calibration model.

Table 5. Prediction result of each sample set with the combined calibration model for harvest years.

Calibration		Prediction							
Model	*R*	1995		1996		1997		Combined	
		SEP	Bias	*SEP*	Bias	*SEP*	Bias	*SEP*	Bias
Combined	0.94	0.53	0.005	0.47	–0.117	0.58	0.090	0.53	0.004

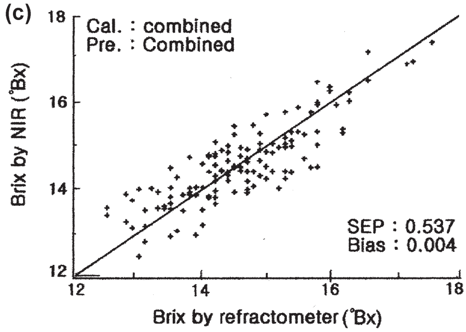

Figure 4. NIR *vs* actual Brix of apple fruit, showing the prediction results of the combined prediction sets with the combined calibration models for the harvest year.

to make a new calibration model every year for each district. A great deal of effort should be made to establish a robust calibration.

Conclusion

A robust calibration model for determining sweetness of apple fruit was developed using near infrared spectroscopy and the influences of growing district and harvest year were investigated. The calibration model for each growing district predicted was well predicted to their own sample set but poorly predicted to the other sample sets. The combined calibration model for three growing districts predicted samples reasonably well with an *SEP* of 0.69% and a bias of –0.075%. The calibration model for each harvest year was not transferable across harvest years but the combined calibration model for three harvest years was sufficiently robust to predict each sample set (*SEP* = 0.53%, bias = 0.004).

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