A Simple Method of System Response Compensation of a Near Infrared Instrument for Determining Brix Value of Peaches

Karunrat Sakulnarmrat[1*] Piyamart Jannok[2,3] Tomoyuki Shinomiya[3]
Yoshinori Kamitani[3] and Sumio Kawano[3]

[1]Faculty of Agriculture and Technology, Rajamangala University of Technology Isan, Surin 32000

[2]Faculty of Engineering and Architecture, Rajamangala University of Technology Isan, Nakorn Ratchasima 30000

[3]Faculty of Agriculture, Kagoshima University, Ka goshima 890-0065 Japan

Abstract

A system response of a near infrared (NIR) instrument sometimes changes depending on measuring conditions such as warming up time, room temperature and the others. In the last peach experiment, we measured NIR spectra over 3 days and spectral differences were observed between spectra measured at the first day and those at the second and third days. Therefore, a simple method of system response compensation was examined. As a result of principle component analysis (PCA) of second derivative (2D) spectra of peaches, samples were separated into two groups, the first-day measured samples and the second and third-day measured ones on the plane consisted of PC1 and PC2. On the hypothesis that average 2D spectrum of each group should be almost the same, the difference of the average 2D spectra (Δ2D spectrum) was calculated. Using Δ2D spectrum, 2D spectra of the first-day samples were adjusted to those of the other samples. The data set including the adjusted one is called "compensated 2D data set" hereafter as compared with "original 2D data set". As results of partial least square (PLS) regressions based on the original and compensated 2D data sets and Brix value of peaches, good SEPs of 0.98 °Brix for both cases could be obtained. The number of factors for the calibration model in case of compensated 2D data set was smaller than that in case of original one. It was concluded that the method using Δ2D spectrum could be used to compensate the difference of system response of an NIR instrument.

Keywords: Compensation; System Responses; Difference Spectra; NIR

* *Corresponding Author: karunrat@hotmail.com Tel. 09 2558 4004*

1. Introduction

Near Infrared (NIR) Spectroscopy has become increasingly important tool in many manufactures such as food industry, pharmaceutical industry, etc (Kawano, 1994). The NIR technique provides several advantages over conventional method known as a destructive method, time-consuming and chemical-related sample preparation. However, there still remain many challenges when applying this technique in production or quality evaluation. Some of the factors that can influence the NIR method accuracy are generated from various sources such as NIR instrument (e.g. integration time, number of scans, lamp power, sensitivity, resolution, spot size), light scattering, modelling (e.g. pretreatment, calibration, validation, spectral range), measurement (metric composition, operator) and environment (vibration, ambient light, temperature, humidity) (Osborne et al., 1993). In order to minimize instrument effects, these variations have to be taken into account to acquire the optimal and stable model. Pretreatment is a common tool normally applied to the original data in order to eliminate system responses originated NIR instrument effects. The correct use of pretreatment can be of great help to acquire an optimal and stable model. Difference spectra are considered as a potential pretreatment to minimize variability related system response.

Therefore, in this study, the determination of peach Brix value was evaluated by conducting the experiment with different time course (3 days) in order to study the performance of a system response compensation using difference spectra as pretreatment.

2. Materials and methods

2.1 Sample

One hundred and fifty peach fruits (*Prunus persica* Rosaceae) grown in Yamanashi prefecture were purchased from a supermarket during the harvesting time on July 2014, Kagoshima, Japan. Samples were kept in 4°C before the experiment. Samples were gently wiped at the area for spectrum scanning using tissue, labelled and kept in the temperature control room at 25°C overnight prior to spectral acquisition. The 150 peach samples were separated into 3 groups (50 fruits/group) for three day- experiment.

2.2 Spectral acquisition

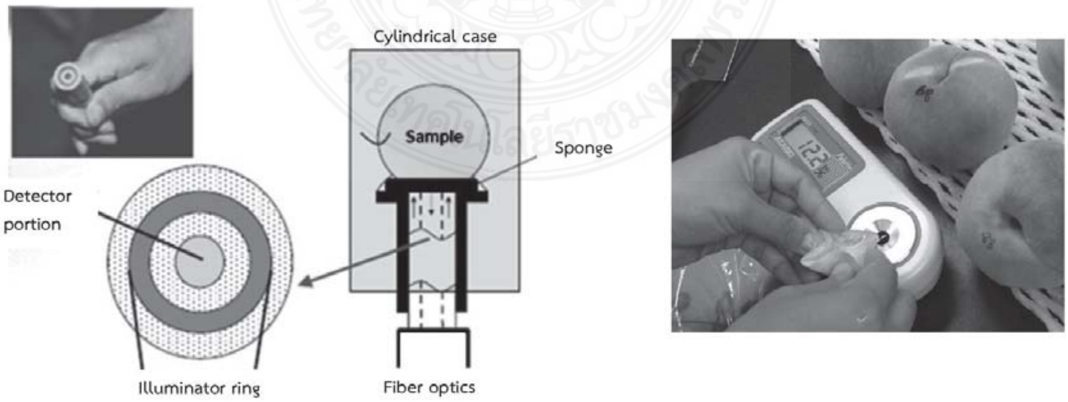
A NIR instrument Model 6500 (Foss NIR Systems, Laurel, MD, USA) was used to measure the NIR spectra (400-1100 nm) of peach samples using the interactance mode (Figure 1A). The interactance probe was composed of a concentric outer ring illuminator and an inner ring detector. Before the spectral acquisition, the samples temperature was controlled at 25°C for at least 30 min using a water bath, covered with a thin polyethylene film. During sample temperature control, the water bath containing samples was also covered with an insulator. A reference measurement was performed with a white ceramic plate every five fruit samples. The NIR measuring conditions were as follows, (1) there were 50 scans per sample, (2) the measuring position of each sample was the equator of the fruit, and (3) during the measurement, each sample was covered with a cylindrical case.

2.3 Data analysis

As for data analysis, the Unscrambler program (version 9.8, CAMO, Japan) were used for principal component analysis (PCA) and partial least squares (PLS) regression. Second derivative (2D) treatment was used as a spectra pre-treatment method. The second derivative treatments were performed with Savitsky-Golay (20 points of each left and right side). The wavelength region used for the PLS regression was selected by trial and error, and fixed to be 790-1058 nm.

2.4 Reference analysis

After the NIR measurement, fruit was immediately cut approximately 7-10 mm depth from the peel at the NIR measuring area. The Brix value of each sample was measured with a digital refractometer (Model PR101, ATAGO, Tokyo, Japan) using juice squeezed by fingers. The triplicate and the two close values were selected and averaged for data analysis. The finger-squeezing are shown in Figure 1B. The reference data were shown in Table 1.



(A) (B)

Figure 1 NIR measurement using interactance mode (A) and Brix value measurement of finger-squeezed juice using digital refractometer (B)

Table 1 Characteristics of calibration and validation samples set of peach

Item	Calibration set	Validation set
Number of samples	74	73
Range (°Brix)	13.6 - 21.2	14.0 - 21.0
Mean (°Brix)	16.9	16.9
SD (°Brix)	1.69	1.63

3. Results and discussion

3.1 NIR Spectra

The average second derivative (2D) spectra of peach samples measured at each experimental date were shown in Figure 2(A). Absorption peaks due to water were observed at 974 nm for first-day and at 972 nm for second-day and third-day. As a same lot of peach samples were used in this experiment, the average 2D spectra should be almost the same. To understand the differences between the group of first-day and the other group of second and third-day, PCA was applied to the 2D spectra of all samples.

3.2 Principle component analysis (PCA)

The PCA score plots on the plane consisted of PC1 and PC2 were shown in Figure 3(A). Clear separation could be observed between the group of first-day and the group of second and third-day. This phenomenon still happened though since the same lot and the same NIR instrument as well as same condition (e.g. warming up temperature, sample temperature, sample preparation) were used. This phenomenon might come from the difference of system response among the experimental days.

3.3 Procedure to adjust the 2D spectra of rst-day samples to ones of second and third-day samples

As mention before, the average 2D spectrum of first-day samples should be the same as that of second and third-day samples. Therefore, 2D spectra of first-day samples were adjusted using the following procedure.

a. Different spectrum between the average 2D spectrum of first-day samples and that of second and third-day samples is calculated, which is called "Δ2D spectrum" hereafter.

b. Each spectrum of first-day samples is adjusted using the Δ2D spectrum.

c. The data set including the adjusted 2D spectra of first-day is called "compensated 2D data set" hereafter as compared with "original 2D data set".

The average 2D spectra for each experimental date calculated from the compensated 2D data set were shown in Figure 2(B) and the result of PCA was shown in Figure 3(B). The differences in both figures were eliminated by using the compensated 2D data set.

Table 2 Results of PLS regression for determining Brix value of peaches

Calibration model	Data set	Wavelength region (nm)	F	R^2	SEC (°Brix)	SEP (°Brix)	Bias (°Brix)
A	Original 2D	790 – 1058	7	0.79	0.77	0.98	-0.05
B	Compensated 2D	790 – 1058	6	0.80	0.76	0.98	-0.06

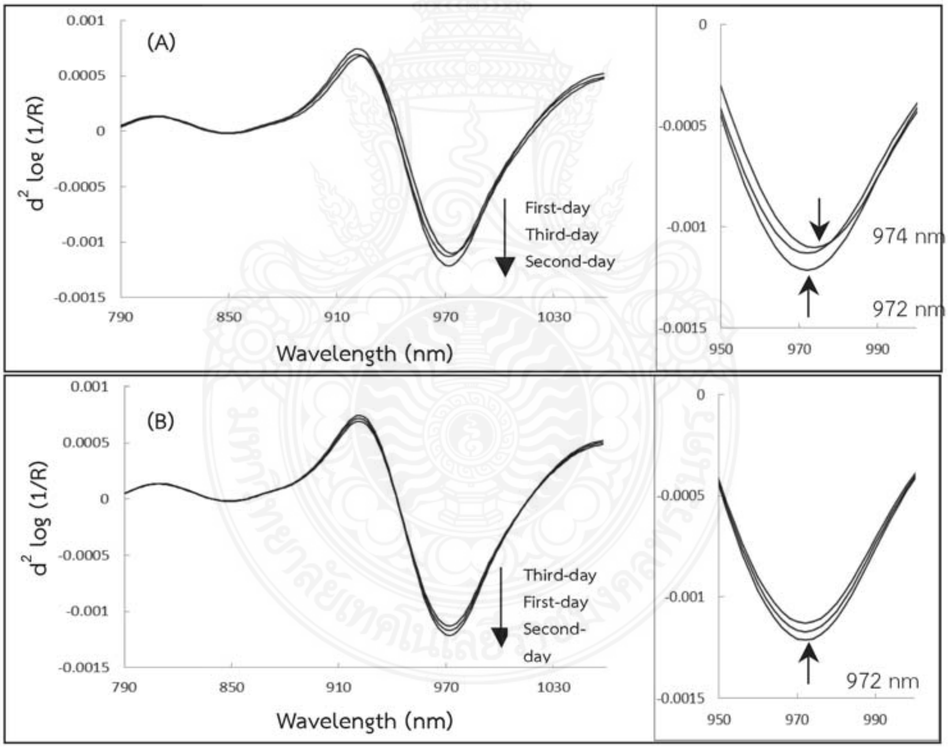


Figure 2 The averaged second derivative spectra of peach fruits calculated from A) original 2D data set and (B) compensated 2D data set

3.4 Calibration models

The calibration model A (model-A) was developed by PLS regression based on the original 2D spectra data set and Brix values. The calibration model B (model-B) was developed by PLS regression based on the compensated 2D spectra data set and Brix values. The results of PLS regression of the two model developed for determining the Brix values of intact peaches are shown in Table 2. The best calibration model could be obtained at 7 factors for former, and at 6 factors for the latter. The SEP was 0.98°Brix for both cases. The Brix value (°Brix) were calculated by using the equation:

$$\text{Brix value (°Brix)} = 14.38 - 223.33A_{790} - 135.20A_{792} + \ldots - 250.30A_{1058}$$

when A_x = second derivative value at wavelength x nm

3.5 Structure of the calibration models obtained

In order to understand the structure of the calibration models obtained, the loading weights for each factor were shown in Figure 4. In the figure, the loading weights connected by the line were similar. The factor 4 of the calibration model-A was independent, indicating that the factor played the role of compensation of difference of system response among the experimental days. In case of calibration model-B, the factor was not needed because the difference of system response was already compensated.

The regression coefficient plots for the calibration model-A and model-B were shown in Figure 5. The shape of the plots for the calibration model-B was simpler than that of the calibration model-A. Because system response compensation by the model was not needed in case of the calibration model-B. When 2D spectra were used for PLS regression, the negative peaks around 910 nm are very important in the regression coefficient plots for Brix value determination because sugar (sucrose) absorption band is located at 918 nm. (Kawano *et al.*, 1992). The Brix value of mangoes could be measured by using 913 nm (Saranwong *et al.*, 2003). Jannok *et al.* (2014) also reported the strong negative peaks of apple, pear, persimmon and common calibration models around 906, 910, 912 and 910 nm, respectively.

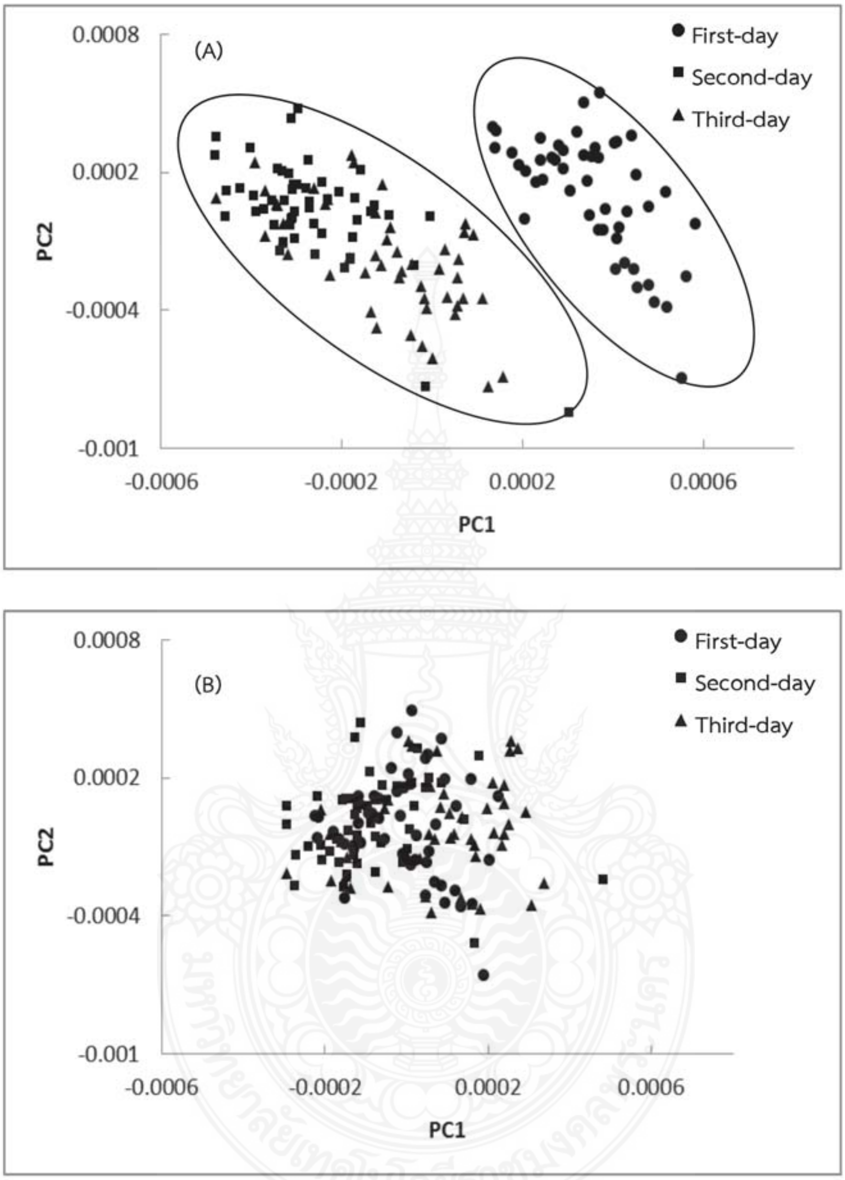


Figure 3 PCA score plots on the plane consisted of PC1 and PC2 calculated from (A) original 2D data set and (B) compensated 2D data set

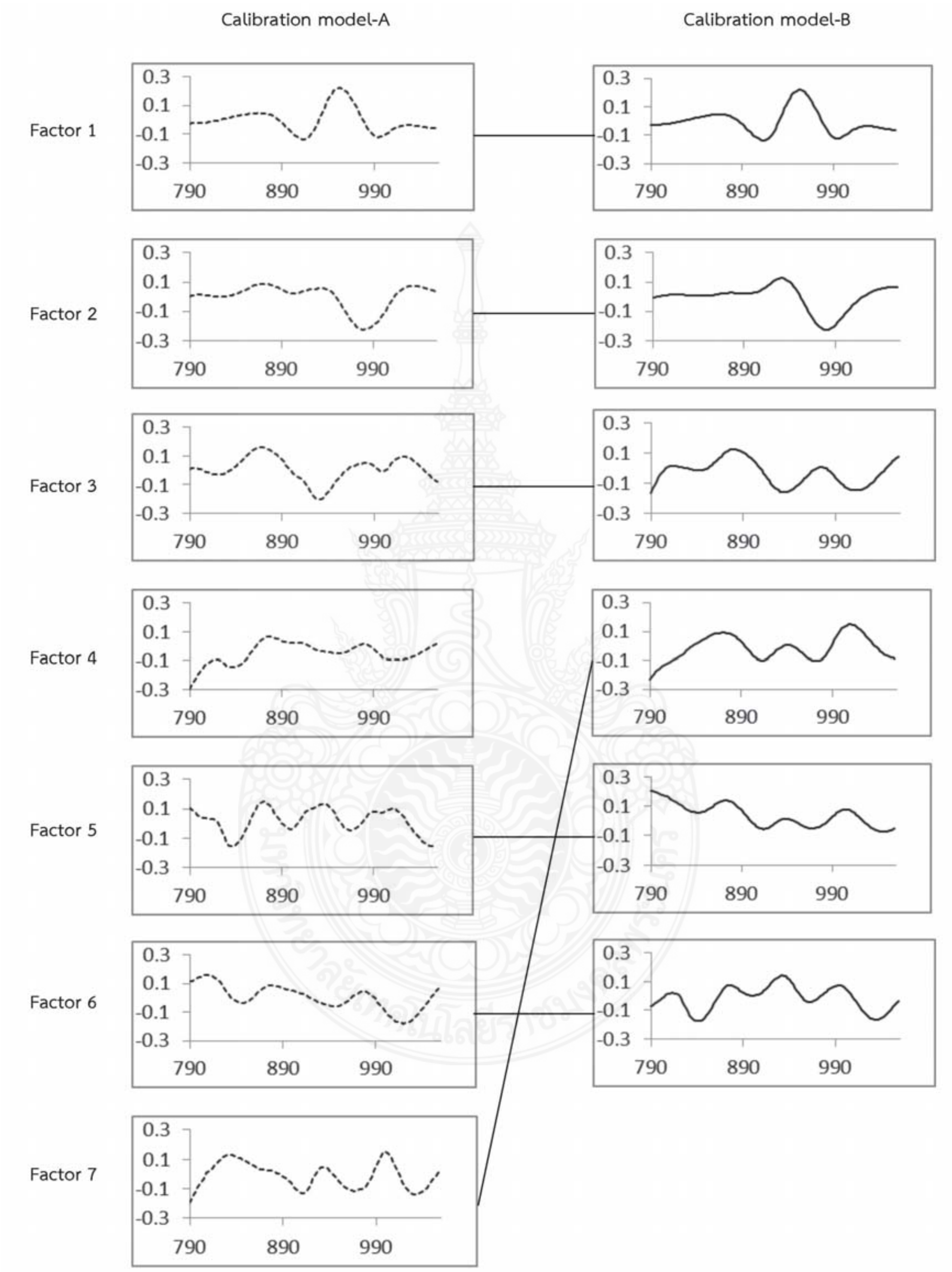


Figure 4 The comparison of loading weight of each factor for calibration model-A and model-B

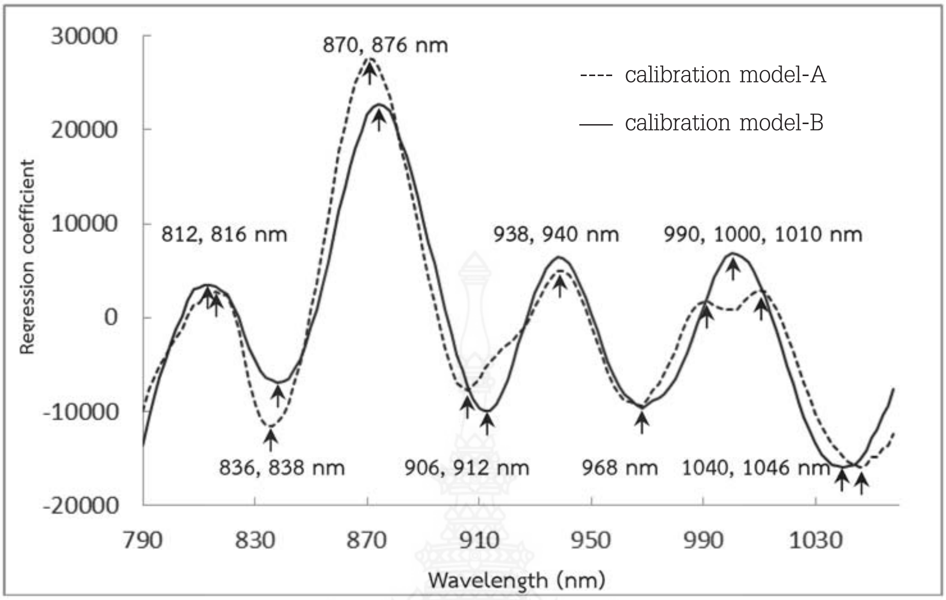


Figure 5 Regression coefficient of calibration model-A and model-B

4. Conclusion

A procedure to compensate the difference of system response of NIR instrument among the experimental days was examined. It was concluded that spectral adjustment of each spectrum using Δ2D spectrum which was a different spectrum between the average 2D spectrum of one group and that the other groups was useful. Therefore, the calibration model developed from this procedure could apply well for determining the Brix values of intact peaches.

5. Acknowledgements

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