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Prediction of ripe-stage eating quality of mango fruit from its harvest quality measured nondestructively by near infrared spectroscopy

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Abstract

A technique to predict eating quality of ripe mango fruit from its harvest quality, measured nondestructively by near infrared (NIR) spectroscopy, was successfully developed. The experiment was conducted in the following steps: (i) identification of the harvest indices (harvest quality) by investigating the relation between physico-chemical properties of hard green mango fruit and those of ripe ones using group sampling; (ii) development of NIR calibration equations to predict the harvest quality of hard green mango fruit nondestructively; (iii) examination of a relation between harvest quality and eating quality of the same fruit, and development of an equation to predict the eating quality from the harvest quality. From the above steps, the results obtained were as follows: (i) dry matter (DM) and starch could be used as harvesting indices for hard green mango fruit as they had a strong relationship with the ripe-stage eating quality (soluble solids content: SSC), while individual sugars and fruit density did not; (ii) the NIR calibration equations developed were sufficiently precise for determining DM and starch of hard green mango fruit (SEP: 0.41 wt.% for DM, 1.71 wt.% for starch); (iii) ripe mango fruit would have excellent eating quality and high SSC if the fruit contained sufficient amounts of DM and starch at harvest date, and the SSC of ripe mango fruit could be precisely predicted from the DM and starch measured nondestructively with NIR at harvest.

Keywords: Harvest index; Maturity; Mango; Near infrared (NIR) spectroscopy; Nondestructive quality evaluation; Eating quality

1. Introduction

Mango fruit are usually harvested at the hard green stage (unripe) when they are physiologically mature but before the onset of the climacteric rise (Lakshminarayana et al., 1970). Mature hard green mango fruit attain a superior eating quality when ripe while immature ones do not (Medlicott et al., 1988). Therefore, discrimination between mature and immature fruit at harvest, and measurement of harvest quality of hard green mango fruit is very important from the marketing point of view.

To determine the harvest quality, accumulation of starch and dry matter (DM) during maturation has been well defined (Tandon and Kalra, 1983; Ueda et al., 2000). An increase in fruit density, or specific

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gravity (SG) was well correlated with eating quality (Kapse and Katrodia, 1997; Kudachikar et al., 2001); however, an argument that this increase is not sufficiently significant has also been made (Del Mundo et al., 1984). Kudachikar et al. (2001), and Ueda et al. (2000) suggested the use of flesh color or flesh carotenoids as maturity indices. For practical applications, Kosiyachinda et al. (1984) recorded some external properties such as the numbers of days after full bloom (DAFB) or days after fruit set (DAFS), shoulder growth, peel color, and an existence of powdery material called "bloom" on the fruit surface; however, these properties may not have a direct impact on the eating quality. On the other hand, chemical properties such as starch or DM might be more appropriate as they are directly related to the eating quality. Nevertheless, measuring the chemical properties is invasive, and thus prohibits the use of the same sample to evaluate eating quality.

As a nondestructive method, near infrared (NIR) spectroscopy has been used to evaluate internal quality of fresh fruits such as peach (Kawano et al., 1992, 1995), satsuma mandarin (Kawano et al., 1993) and mango (Guthrie and Walsh, 1997; Peiris et al., 1999; Schmilovitch et al., 2000). Previous studies have shown that NIR has the capability to evaluate soluble solids content (SSC) and DM in ripe mango fruit (cv. 'Caraboa') (Saranwong et al., 2001, 2003). Thus, if NIR is used to measure harvest quality of hard green mango fruit nondestructively, a study of a relationship between harvest quality and eating quality using the same fruit will be possible.

In this work, the harvest quality of hard green mango fruit was identified, and a technique to predict the ripe-stage eating quality of mango fruit from its harvest quality measured nondestructively by NIR was developed.

2. Materials and methods

2.1. Experiment 1: changes in physico-chemical properties during maturation, and identification of harvesting indices

2.1.1. Samples

A total of 288 mango fruit (*Mangifera indica* cv. 'Mahajanaka') cultivated in Lumpang province, Thailand, were used. To protect the fruit from pests during fruit development, a thin paper bag was used to bag the fruit (open-end bagging). Forty-eight hard green fruit from a set of eight mango trees (i.e., six fruit per tree) were harvested weekly from 105 to 140 days after fruit set, in 2001. After being harvested by hand, the fruit were transported to the laboratory at Chiang Mai University in an air-conditioned car, and the fruit kept in the laboratory for at least 1 h before further analyses.

At the laboratory, the hard green mango fruit were separated into two equal groups distributed across the trees. In the first group, the fruit were used for analyses of harvest quality. In the second group, the fruit were kept in storage at 25 °C in a similar way to practical marketing procedures. Calcium carbide, an acetylene-releasing agent, was applied to the fruit in this group to stimulate ripening. Eating quality of the ripe fruit was evaluated after a 5-day storage period.

2.1.2. Analysis of physico-chemical properties of hard green mango fruit

Fruit density, peel color, flesh color, dry matter, starch and individual sugar contents were measured. The measurements of fruit density, peel color, flesh color and DM content were done at the harvest date. Starch and individual sugars were measured later from dried and frozen samples, respectively. For each harvest date, all 24 fruit were used for the determinations of all physico-chemical properties mentioned above except that of starch for which 16 fruit were used. The values of peel color, flesh color and amount of DM were calculated from the average of duplicate determinations, while the value of fruit density, amounts of starch and sugars were calculated from a single determination.

Density was measured by measuring fruit weight in air and in water. Peel color and flesh color, expressed as Hunter *L*, *a* and *b* values, were measured at the fruit shoulder with a color meter model "CR-200" (Minolta, Osaka, Japan). The *L*, *a* and *b* values obtained were transformed to hue angles after McGuire (1992).

A portion of flesh at the shoulder position (about 5 cm diameter and 10 mm deep) was taken and analyzed for DM by drying it at 70 °C for 48 h. Subsequently, the dried sample was milled through a 0.5 mm screened mill "Cyclotec" (Foss Tecator AB, Hoganas, Sweden) for starch analysis with the "total

starch assay kit" (Megazyme, Catalog No. K-TSTA, Wicklow, Ireland).

For sugars, the amounts of glucose, fructose and sucrose were measured. A portion of flesh (about 1 g) from another shoulder of the fruit was taken and frozen. The sugars were extracted by homogenizing the sample with 10 ml of water. Suspended solids were filtered with the Millipore filter model "Biomax-10" (10,000 nominal molecular weight limit) at 5000 g for 90 min. Ten microliters of aliquot was injected into a high performance liquid chromatography (HPLC) model "10AD series" (Shimadzu, Kyoto, Japan) to measure concentrations of each sugar. The HPLC was operated under the following conditions; column: Shimpack SCR-10N; mobile phase: water; flowrate: 0.8 ml/min; column temperature: 60 °C; detector: RI.

2.1.3. Evaluation of eating quality of the ripe mango fruit

After a 5-day storage period at 25 °C, the ripe mango fruit were evaluated for their eating quality by a trained panel, into three categories: (A) excellent; (B) not excellent but acceptable; and (C) unacceptable. Soluble solids content, titratable acidity (TA) as percentage citric acid, and flesh firmness of the fruit were determined by a digital refractometer, titrating with 0.1 M NaOH and a hand penetrometer with a round measuring head (7.9 mm diameter, 6.9 mm depth), respectively. Colors of peel and flesh were determined colormetrically as described earlier. Color and SSC were calculated from the average of duplicate measurements. TA and flesh firmness were based on a single measurement.

2.1.4. Data analysis

Analysis of variance (ANOVA) with randomized complete block (RCB) using mango trees as a block was performed by SPSS® (SPSS, Illinois, USA). Tukey's least significant difference (LSD) was used to test the significant difference at the 95% confidence level of each variable.

2.2. Experiment 2: nondestructive measurement of harvesting quality with NIR

2.2.1. Samples

A total of 197 mango fruit (cv. 'Mahajanaka') cultivated in the same orchard as for experiment 1 were used. The hard green mango fruit was harvested weekly from 98 to 147 DAFS, in 2002. The harvesting and transportation procedures were similar to those described in experiment 1.

2.2.2. Spectral acquisition

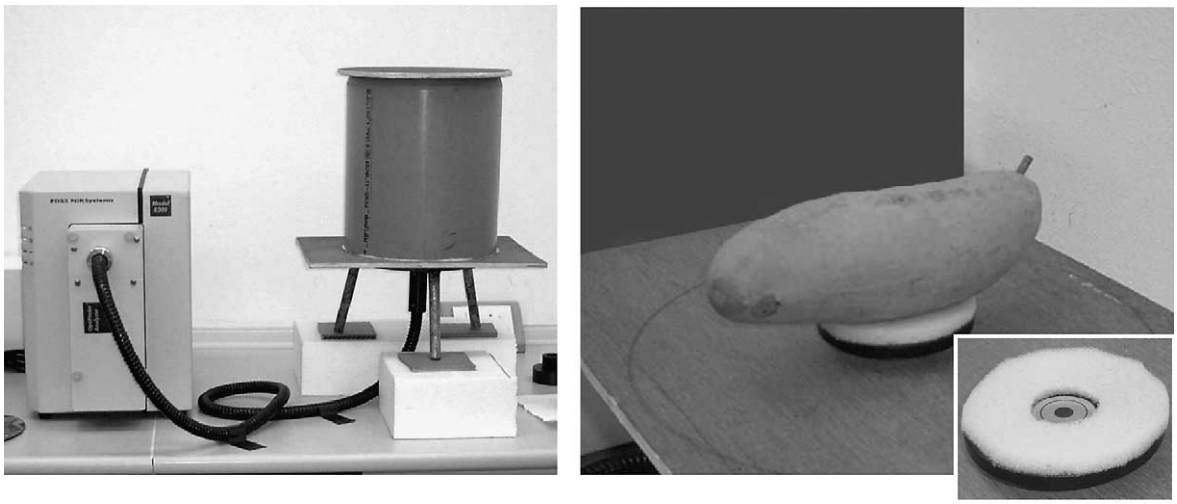
At the harvest date, NIR spectra of the hard green mango fruit were measured in a short wavelength region from 700 to 1100 nm. A commercially available NIR spectrophotometer "NIRS6500" (Foss NIRSystems, Silver Spring, USA) with a fiber optic "interactance probe" (Fig. 1) was used. The sample was positioned in a light-tight polyethylene tube in a similar way to our previous study (Kawano et al., 1992). The geometry of the "interactance" probe used can be found in Saranwong et al. (2003). The NIR spectrum was obtained at the fruit shoulder by averaging 50 scans (total measuring time = 25 s). A reference measurement of a teflon cylinder (10 cm diameter, 11 cm height) was performed after seven samples. A control of sample temperature at 25 °C prior to NIR measurement was done as described in Saranwong et al. (2001).

2.2.3. Chemical analyses

Within 30 min after spectra acquisition, a portion of the flesh of each fruit which was illuminated by NIR radiation (about 5 cm diameter and 10 mm deep) was taken and analyzed for DM, and subsequently for starch contents as described in experiment 1.

2.2.4. Data analysis

For all NIR calculations, samples were manually separated into calibration and validation sets in the same manner as in our previous work (Kawano et al., 1992). Statistical characteristics of the calibration and validation sets are given in Table 1. Spectra pretreatments of multiplicative scattering correction (MSC), second derivative (segment = 4 nm, gap = 4 nm) and their combination were applied to the spectra to obtain the best calibration result. Multiple linear regression (MLR) and partial least squares (PLS) regression were used to develop calibration equations. Near Infrared Spectral Analysis Software (NSAS®) (Foss NIRSystems) was used for calculation of second derivative and MLR (manual wavelength selection by the step-up algorithm). The Unscrambler® (CAMO, Oslo, Norway) was used for MSC and PLS calculations.



(a) (b)

Fig. 1. Sample presentation for NIR spectral acquisition of mango fruit. (a) The spectral acquisition system consists of the NIR spectrophotometer, the fiber optic with 'interactance' probe and the light-tight tube. (b) A mango fruit positioned for spectral acquisition with the 'interactance' probe (insert).

2.3. Experiment 3: prediction of eating quality using NIR-predicted harvesting quality

A total of 151 mango fruit (cv. 'Mahajanaka') harvested under the same conditions as described in experiment 2 were used.

The values of harvest quality of hard green mango fruit were measured nondestructively by the NIR calibration equations developed in experiment 2. The eating quality of the same sample after 5-days storage was evaluated. The significant differences at 95% confidence of quality attributes of the immature and mature groups were tested by a *t*-test using the SPSS program.

For the calculation of SSC prediction equations from the NIR-predicted harvesting quality, samples were manually separated into a calibration set ($n = 77$) and a validation set ($n = 74$) as described in experiment 2.

Table 1
Characteristics of calibration and validation sample sets of mango used to develop calibration equations with temperature compensation

Items	Dry matter		Starch	
	Calibration set	Validation set	Calibration set	Validation set
N[a]	104	87	102	94
Range	15.7–23.5	16.5–22.4	33.0–52.6	34.5–52.4
Mean	19.55	19.39	42.79	42.75
S.D.[b]	1.51	1.26	4.46	4.08
Unit	wt.%		wt.% (dry weight basis)	

[a] *N* is the number of samples for one temperature.
[b] S.D. calculated from a set of sample with single temperature. The difference between S.D. from single temperature set and three-temperature set was negligible.

3. Results and discussion

3.1. Experiment 1: changes of physico-chemical properties during maturation, and identification of harvest indices

Table 2 shows physical and chemical properties of hard green mango fruit harvested at various harvest dates. Peel color did not show a significant trend during maturation while flesh color changed from white to bright yellow in the late harvested fruit. Fruit density rose slightly when it was harvested later, but by less than 0.01. Significant increases in DM and starch contents during maturation were found, while there were no significant differences in total sugar, reducing

Table 2
Physico-chemical properties of hard green mango fruit harvested at each harvest date

H date (DAFS)[a]	Color (°Hue)		SG[b]	DM[c] (wt.%)	Starch (wt.%, dry base)	Sugar (wt.%, wet base)[d]				
	Peel	Flesh				Glc	Frc	Suc	Red	TS
105	118.9 ab[e]	95.4 a	1.005 a	16.89 a	46.31 a	0.16 a	1.64 ns	1.48 ns	1.80 ns	3.28 ns
112	120.2 a	93.9 b	1.009 abc	17.61 a	50.69 b	0.13 ab	1.69	1.45	1.82	3.26
119	119.8 ab	93.1 bc	1.007 ab	17.63 a	52.95 bc	0.10 bc	1.61	1.51	1.71	3.22
126	117.8 b	92.5 cd	1.012 bc	19.06 b	54.81 c	0.11 bc	1.78	1.47	1.89	3.36
133	119.5 ab	92.0 de	1.012 bc	18.80 b	55.11 c	0.09 c	1.68	1.48	1.77	3.25
140	118.7 ab	91.5 e	1.014 c	19.22 b	55.17 c	0.09 c	1.72	1.71	1.81	3.52

[a] Harvest date (days after fruit set).
[b] Specific gravity.
[c] Dry matter.
[d] Glc: glucose; Frc: fructose; Suc: sucrose; Red: reducing sugar (glucose + fructose); TS: total sugar (glucose + fructose + sucrose).
[e] Significant difference at 95% interval tested by Tukey's least significant difference with randomized complete block design.

sugar, fructose and sucrose contents. Glucose content decreased slightly during maturation, however this amount was too small to affect the total sugar changes.

For eating quality, it was found that the percentage of fruit having excellent eating quality increased in late harvested fruit, more than 75% for the fruit harvested at 133 and 140 DAFS. Corresponding to the sensory evaluation, SSCs of the fruit harvested at 133 and 140 DAFS were higher than those harvested earlier (Table 3). TA and peel yellowness of those late harvested fruit also were higher than for the earlier harvested ones, but there were no significant differences in flesh color and firmness throughout maturation.

Tables 2 and 3 show that DM and starch contents at harvest had a high relationship with eating quality. Fruit harvested at 133 and 140 DAFS had significantly higher levels of DM and starch compared with others, and also had superior eating quality. Selection of DM and starch as harvesting indices was thus appropriate since starch was the source of sugar production at the ripe stage. Accumulating a sufficient amount of starch would allow the ripe fruit to be able to synthesize a large amount of sugar. This is supported by significant activities of starch breakdown and sugar synthesis enzymes during ripening (Tandon and Kalra, 1983; Ueda et al., 2000). The increase in DM suggests accumulation of organic substances needed for completing the ripening process. While there was a change in flesh color during maturation, flesh color or carotenoid substances were not directly related to eating quality. Moreover, using flesh color as a harvest index might easily lead to problems with immature fruit, since this property is easily manipulated by cultural practice, such as fertilizers. The inapplicability of fruit density was due to the relatively small air cavity between the seed and endocarp in this cultivar, as it is the main cause of density change in other mangoes (Jaipet et al., 1987). The fact that the

Table 3
Eating quality of ripe mango fruit harvested at each harvest date

Harvesting date (DAFS)	Color (°Hue)		SSC (°Brix)	TA (wt.%/v)	Brix:TA	Firmness (*N*)
	Peel	Flesh				
105	84.81 a[a]	79.08 ab	13.84 a	0.29 a	49.30 ab	7.46 a
112	84.04 a	79.24 ab	14.69 b	0.28 a	54.20 b	9.10 b
119	83.66 a	78.40 a	15.13 b	0.28 a	54.24 b	7.23 a
126[b]	–	–	–	–	–	–
133	80.54 b	79.65 b	16.42 c	0.37 b	45.86 a	7.51 a
140	80.25 b	79.68 b	16.64 c	0.34 b	49.74 ab	7.75 a

[a] Significant difference at 95% interval tested by Tukey's least significant difference with randomized complete block design.
[b] Data missing due to the mis-application of calcium carbide.

sugar contents did not change during maturation was probably due to catabolism of incoming sugars from the leaves, as indicated by activity of invertase during maturation (Rahman et al., 1997).

Therefore, based on the above evidence, DM and starch were selected as harvesting indices to be measured nondestructively by NIR.

3.2. Experiment 2: nondestructive measurement of harvest quality with NIR

Original [log(1/*R*)] and second derivative [d^2 log (1/*R*)] spectra of typical hard green mango fruit having low, medium and high values of DM and starch contents are shown in Fig. 2. The log(1/*R*) values of each fruit seemed to be affected by scattering conditions in the sample rather than DM and starch contents. This phenomenon is typical in NIR where the light pathlength cannot be controlled (Osborne et al., 1993). In the second derivative spectra, the strong absorption bands at 840 and 962 nm were caused by water absorption.

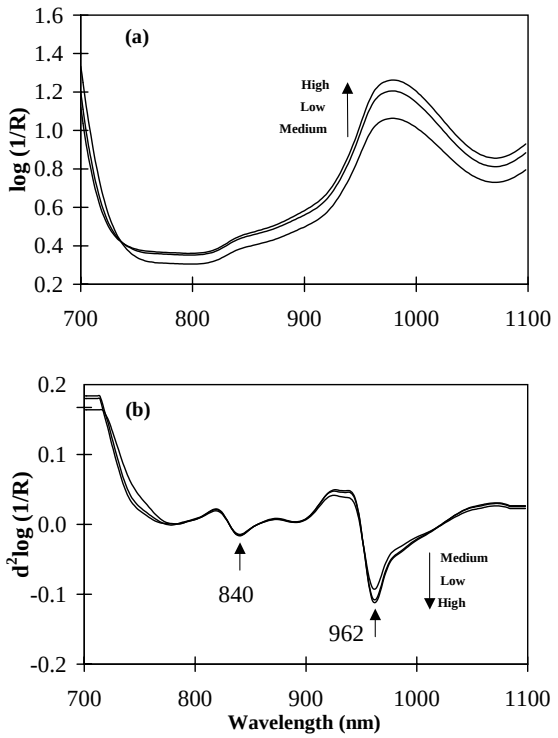


Fig. 2. Original spectra (a) and second derivative spectra (b) of typical hard green mango fruit having low, medium and high DM and starch contents.

Table 4
Calibration and validation results for determining DM and starch of mango fruit

Constituent	F[a]	R	SEC	SEP	Bias
DM[b]	4	0.96	0.44	0.41	0.07
Starch[c]	8	0.93	1.64	1.71	−0.22

R: multiple correlation coefficients; SEC: standard error of calibration; SEP: bias-corrected standard error of prediction; Bias: the average of difference between actual value and NIR value.

[a] *F* is the number of the wavelength used for the MLR calibration and the number of the factor used for the PLS calibration equation.

[b] Calibration and validation results from MLR calibration on MSC-treated second derivative spectra. The wavelengths of 914, 882, 826 and 954 nm were used for the calibration equation.

[c] Calibration and validation results from PLS calibration on second derivative spectra. The wavelength region of 850–1000 nm was used for the calibration equation.

Calibration results for determining DM and starch contents are shown in Table 4. For DM calibration, MLR calibration based on MSC-treated second derivative spectra (MSC was applied to the original spectra first, followed by second derivative treatment) provided the best result. The pretreatment condition used and calibration accuracy was similar to that in our previous work on ripe 'Caraboa' mango fruit (Saranwong et al., 2001). The wavelength of 914 nm was used as the first wavelength in the calibration equation. The slight shift of this first wavelength from our previous study at 906 nm might be due to the condition of fruit which were hard green instead of ripe. However, using this wavelength as the first wavelength in the model was reasonable as it was the absorption band of starch (data not shown) or other carbohydrates, not that of water (Kawano et al., 1992). Wavelengths of 882, 826 and 954 nm were used as second, third and fourth terms in the calibration equation, respectively.

For starch determination, PLS calibration on second derivative spectra (wavelength region: 850–1000 nm) provided the best result. Eight factors were used for the PLS regression equation. The accuracies of the developed calibration equations with SEPs of 0.41% for DM and 1.71% for starch were considered to be sufficiently accurate as they were about two times smaller than the differences of the DM and starch contents between the immature and the mature fruit (Table 2).

Table 5
Harvest quality and eating quality of immature and mature mangoes

Items	Harvesting quality[a]		Eating quality[b]		
	DM (wt.%)	Starch (wt.%, dry base)	SSC (°Brix)	TA (wt.%/v)	Firmness (*N*)
Immature ($n = 69$)	18.54 a[c]	39.40 a	13.42 a	0.38 ns	10.20 a
Mature ($n = 43$)	21.15 b	46.76 b	16.46 b	0.36	8.07 b

Harvest quality at the hard green stage and eating quality at the ripe stage were measured on the same samples.
[a] Values of harvest quality were predicted by the NIR calibration equations (data shown in Table 4).
[b] Values of eating quality were measured by conventional destructive methods after a 5-day storage period at 25 °C.
[c] Different letter means significant difference at 95% confidence by *z*-test.

Using a 95% confidence paired *t*-test, there were no significant differences between the chemical values and NIR-predicted values in both DM and starch determinations, indicating there was no bias offset.

3.3. Experiment 3: prediction of eating quality using NIR-predicted harvest quality

Harvest quality, DM and starch contents were predicted nondestructively with the NIR calibration equations mentioned above (Table 4). The eating quality of the same fruit was measured later conventionally after ripening. Table 5 shows that the mature fruit (excellent eating quality) had significantly higher amounts of DM, starch and SSC than the immature ones (unacceptable eating quality). Flesh firmness of immature fruit was slightly harder than that of mature ones. No significant differences could be found in TA.

The higher DM and lower starch contents reported in this experiment compared with those of experiment 1 (Table 2) were caused by the difference in sampling procedure. In this experiment, the peel was not removed from the sampled portion to avoid an error in NIR calibrations such as moisture loss after peeling and non-uniform thickness of the peel removed. On the other hand, the peel was removed conventionally in experiment 1. The peel contained higher DM and lower starch contents than the flesh (data not shown). Therefore, including peel in the sampled portion caused the increase in DM and the decrease in starch contents.

As shown in Table 5, it seemed that the fruit having high DM and/or starch contents at harvest would have high SSC when ripe. To predict the SSC from the harvest quality, linear regressions (LR) and multiple linear regressions were applied to the DM and/or starch contents as independent variables (x_{ij}), and SSC as a dependent variable (y_i). Since DM and starch contents were correlated ($R = 0.69$), a validation set was used to evaluate the stability of the developed equations. Calibration and validation results are shown in Table 6. It was found that even the independent variables are correlated; using both of them (calibration A) provided a better prediction result than using only one index (calibration B, C). Scatter plots for the "calibration A" between the actual and predicted SSC of validation sample sets are shown in Fig. 3. The "calibration A" with the SEP of 0.55 °Brix was sufficiently accurate for marketing since the typical customer can discriminate the sweetness of fruit by about 1 °Brix.

To clarify the importance of each harvest index on the SSC calibration equation, the structure of the equation was investigated. The effect of the constituent unit on regression coefficients was removed by subtracting the mean value from the original value of each harvesting index, and then divided by its standard deviation. The SSC calibration equation using unit-corrected harvesting indices can be written as follows:

$$\mathrm{SSC} = 14.755 + 0.812\,\mathrm{DM_c} + 0.677\,\mathrm{starch_c}$$

Table 6
Calibration and validation results for determining SSC of mango fruit at the ripe stage from DM and/or starch of the same fruit at the hard green stage

Calibration	Independent variables[b]	*R*[a]	SEC	SEP	Bias
A	DM and starch	0.92	0.61	0.55	0.16
B	DM	0.86	0.81	0.73	0.09
C	Starch	0.82	0.90	0.77	0.19

[a] *R*: multiple correlation coefficient or correlation coefficients; SEC: standard error of calibration; SEP: bias-corrected standard error of prediction; Bias: the average of difference between actual value and predicted value.
[b] Values were predicted nondestructively by the NIR calibration equations (data shown in Table 4).

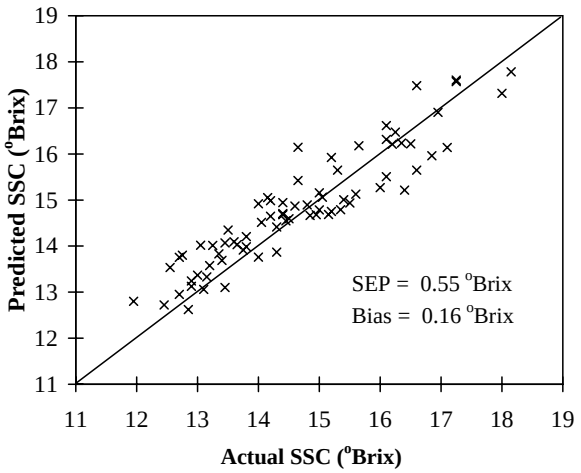


Fig. 3. Scatter plots of actual soluble solids content (SSC) at ripe stage and predicted SSC calculated from NIR-predicted DM and starch contents of the same fruit at the hard green stage.

where DM_c and $starch_c$ are the unit-corrected DM and starch contents, respectively.

From close values of regression coefficients of DM and starch contents shown in the equation, the hypothesis that DM and starch contents were similarly important for predicting ripe-stage SSC was confirmed.

The results show that NIR is a promising technique providing the opportunity for a researcher to investigate the relationships of chemical constituents of the same fruit at different developmental stages. With this newly developed method, a trend-estimation of quality changes during fruit development based on sampling of different samples is no longer needed.

4. Conclusion

It was concluded that DM and starch contents in the flesh of hard green mango fruit at harvest were important factors affecting eating quality of the fruit when ripe. The NIR calibration equations developed were sufficiently accurate to determine the harvest quality, DM and starch content, of hard green mango fruit nondestructively. By the NIR-predicted DM and starch contents of hard green mango, ripe-stage SSC, which was an index for the eating quality when ripe, could be precisely predicted at the harvest date.

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