

Non Destructive Prediction of pH in Mango Fruits cv. Gedong Gincu Using NIR Spectroscopy

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Abstract— Near infrared (NIR) spectroscopy techniques have shown promise as rapid and non-destructive tools to evaluate the various internal quality attributes of fruits. In mango fruits cv Gedong Gincu, acidity (pH) is one of the main quality attribute. Prediction of acidity in mango fruits is generally carried out destructively. The objective of this study was to develop calibration model and prediction of pH in mango fruit cv. Gedong Gincu using NIR spectroscopy. The transmission spectra of mango fruits were obtained in the wavelength range from 1000 to 2400 nm. The prediction model was developed by partial least square (PLS) regression. The coefficient of correlation (r) of pH was 0.9042 and the standard error of prediction (SEP) was 0.12, respectively. It is concluded that by using the NIR measurement system, in the appropriate spectral range, it is possible to nondestructively predict the pH of mango fruit.

Index Term— Non destructive prediction, pH, near infrared spectroscopy, mango fruits cv. Gedong Gincu

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I. INTRODUCTION

Mango fruits (*Mangifera indica* L.) cv. Gedong Gincu is one of exotic tropical fruits from Indonesia. This cultivar has potentially a good price in the world market due to its sweet taste, medium size and beauty orange color. To ensure the

supply of high-quality fruit, it is important to select fruit with the proper degree of maturation. Various scientists have considered maturity from different perspectives [1]. Acidity (pH) is one of the internal quality indices for mango fruits. The methods to measure this internal quality is still destructive. Therefore, it is essential to develop efficient and non-destructive methods for measuring the internal attributes of fruit such as acidity (pH).

Near infrared (NIR) spectroscopy is a fast, easy-to-use and non-destructive analytical technique [2]. NIR spectroscopy has decisive advantages compared to traditional methods, whereby it analyse sample rapidly (a few seconds per sample) and no need sample preparation [3]-[5]. In addition, it is a chemical-free (limited to the reagents required for reference analyses and no waste is produced [4][6] and can be carried out on-line [5].

The use of NIR spectroscopy to measure internal quality attributes of fruits produce has been investigated extensively during the last decade. Use of NIR spectroscopy in fruit is receiving extensive research effort, and commercial applications are in the early stage of implementation [7]-[10]. The ability to rapidly 'scan' fruit on-line, and then sort it, means that if a given characteristic can be accurately measured, fruit can be segregated into distinct classes and either handled or marketed in a different manner. The variety of studied fruit is large, ranging from apple [11]-[13] to melon and pineapple [14], kiwi fruit [15]-[18], citrus [19], mango [20], mandarin [21] [22], peach [23] and pear [24]. More applications and recent developments have been reviewed [25].

Relating spectral data to quality attributes is usually done by partial least square regression (PLS) which refers to the computation of the optimal least-squares fit to part of a correlation or covariance matrix. PLS is quite similar to principal components regression (PCR), but defines the latent variables (principal components) based on the covariance between the independent and dependent variables, rather than on the variance in the independent variables alone [26]. Therefore, the objective of this study was to develop calibration model and prediction of pH in mango fruit cv. Gedong Gincu using NIR spectroscopy. The prediction model was developed by PLS regression.

II. MATERIAL AND METHOD

A. Sample Preparation

The 306 mango fruits cv. Gedong Gincu used in this study were randomly divided into two groups of samples: the first

group was used to develop the calibration models (204 samples) and the other for predicting quality and model validation purposes (102 samples). All samples had been harvested from the same farmer orchard during one day at commercial maturity or at the level maturity of 80-85 percent. After acquisition of spectra, pH measurement was carried out using a digital pH meter (D-24, HORIBA).

B. NIR Spectroscopy Analysis

Spectra of mango fruits were collected in the range of 1000–2400 nm with an increment of 5 nm using NIRFlex N-500 (Büchi Labor Technik AG, Flawil, Switzerland) at room temperature of 25°C. Spectra data were collected by measuring the diffuse reflectance of samples. Operation of the instrument and data collection of NIR spectra were conducted by using NIRWare 1.2 software (Büchi Labor Technik AG, Flawil, Switzerland). Chemometric analysis was conducted by using NIRCal 5.2 software (Büchi Labor Technik AG, Flawil, Switzerland).

A large amount of spectral data is usually obtained from NIR instruments and yields useful analytical information [27][28]. However, the data acquired from NIR spectrometer contains background information and noise besides sample information. In order to obtain reliable, accurate and stable calibration models, it is necessary to pre-process spectral data before modeling [29]. Spectral pre-processing techniques are required to remove any irrelevant information including noise, uncertainties, variability, interactions and unrecognized features. Determining of pre-treatment method to develop calibration model of NIR depends on material type and content to be predicted [30]. Pre-treatment normalization between 0 and 1 method could reduce baseline variation. Spectra variation caused by different grain size distributions could be reduced by normalization of spectra [31]. In this study, pre-treatment normalization between 0 and 1 was used to spectral pre-processing technique.

C. Calibration Model

Calibration model was established using PLS algorithm. Statistical parameters used to evaluate the developed NIR calibration model were:

- 1) Bias, i.e., the average deviation between the reference value (x_n) and the predicted value (y_n) of V-Set. It is recommended that Bias should equal to zero [32].

$$\text{Bias} = \frac{1}{n} \sum (x_n - y_n) \quad (1)$$

- 2) The standard error of calibration set (SEC), i.e., the standard deviation of the differences between the reference value (x_n) and the predicted value (y_n) of C-Set, corrected for bias.

$$\text{SEC} = \sqrt{\frac{1}{n-1} \sum (x_n - y_n - \text{Bias})^2} \quad (2)$$

- 3) The standard error of validation set (SEP), i.e., the standard deviation of the differences between the reference value (x_n) and the predicted value (y_n) of V-Set, corrected for bias.

$$\text{SEP} = \sqrt{\frac{1}{n-1} \sum (x_n - y_n - \text{Bias})^2} \quad (3)$$

- 4) Coefficient of correlation (r) between the reference value (x_n) and the predicted value (y_n).

$$r = \frac{\sum (x_n - \bar{x}_n)(y_n - \bar{y}_n)}{\sqrt{\sum (x_n - \bar{x}_n)^2 \sum (y_n - \bar{y}_n)^2}} \quad (4)$$

The model is considered more useful when r value approaches 1, whereby r value is larger than 0.90, considered as high correlation [32].

- 5) Coefficient of determination (R^2) between the reference value (x_n) and the predicted value (y_n).

$$R^2 = \left(\frac{\sum (x_n - \bar{x}_n)(y_n - \bar{y}_n)}{\sqrt{\sum (x_n - \bar{x}_n)^2 \sum (y_n - \bar{y}_n)^2}} \right)^2 \quad (5)$$

- 6) Coefficient of variation (CV);

$$\text{CV in C-Set: } CV = \frac{\text{SEC}}{\bar{x}} \times 100 \quad (6)$$

$$\text{CV in V-Set: } CV = \frac{\text{SEP}}{\bar{x}} \times 100 \quad (7)$$

A very reliable calibration could be achieved when the value of CV in C-Set was lower than 5% and the value of CV in V-Set was lower than 10% [33].

III. RESULTS AND DISCUSSION

Reference data of pH in sample of mango fruits for calibration set and validation set are shown on Table I. For calibration set, the range of pH was 2.98-4.78 with standard deviation of 0.39. For validation set, pH was 3.03 to 4.56, with standard deviation of 0.37.

TABLE I
REFERENCE VALUES OF pH IN MANGO FRUITS

	n	Minimum	Maximum	Mean	SD
Calibration	204	2.98	4.78	3.42	0.39
Validation	102	3.03	4.56	3.40	0.37

A. NIR Spectra Analysis

Fig. 1 and 2 show original spectra and pre-treatment spectra of pH in mango fruits. The original one shows that there is a parallel shift of spectra. It occurred because spectra data of NIR did not only contain sample information, but also background information as well as noises. Therefore, pre-treatment was needed before modelling to get reliable, accurate and stable calibration model [29]. Spectra data resulted from diffuse reflectance measurement at solid sample would be followed by scattering noise as a result of particle size difference [34]. This case was supported by [27] who acknowledged that physical properties of solid samples influence spectra of solid samples. Spectra pattern of near infrared reflectance indicated that wavelength of 1215-1395 nm was CH_2 , 1450 nm and 1940 nm were water, 1765 nm was CH_2 and cellulose, and 2252-2400 was carbohydrate.

B. Calibration model

Calibration and validation of NIR spectra were carried out to predict pH of mango fruits. Calibration was obtained based on the correlation between data of NIR reflectance with pH (Table 2). For calibration set, it was obtained that Bias, SEC, CV and R^2 were -0.0022, 0.03, 0.97% and 0.99, respectively. For prediction set, it was obtained for Bias, SEP, CV and R^2 were 0.039, 0.012, 3.36% and 0.86, respectively. The result showed that the model has a good correlation. This value was good as [30] stated that calibration model having value of R^2 between 0.66 and 0.81 indicated approximate quantitative

predictions, between 0.82 and 0.90 was considered to be a good prediction, and larger than 0.91 revealed excellent.

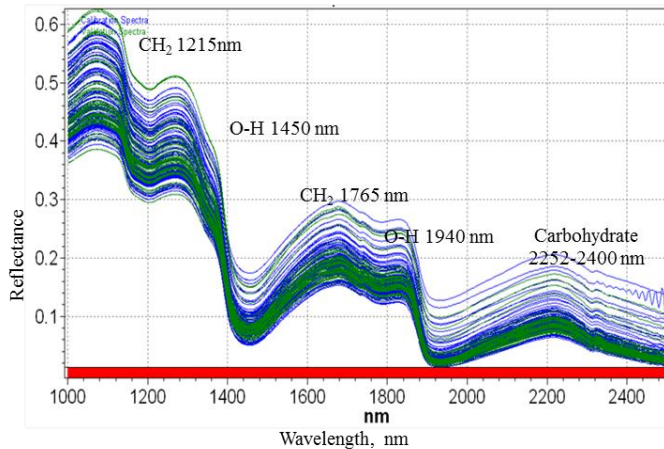


Fig. 1. Original reflectance NIR spectra of mango fruits

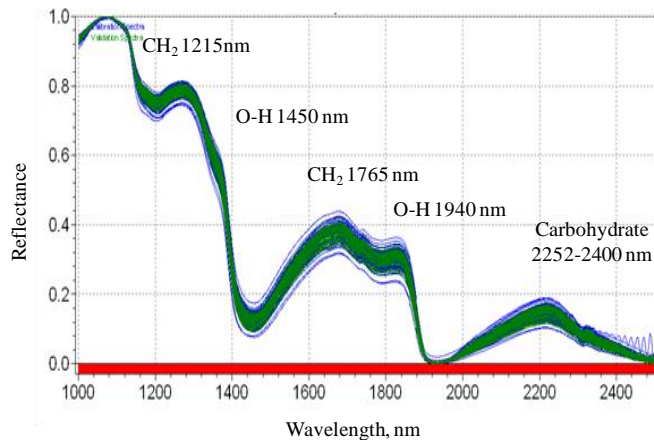


Fig. 2. Normalized reflectance NIR spectra of mango fruits

SEC and SEP value in this study has a quite small. This result was good since there was a small difference between SEC and SEP values. Good calibration model has a small difference between SEC and SEP, meanwhile, a large difference is an indication of calibration set of not a representative of validation set [35]. When SEP value is larger than two times than SEC, most likely over fitting will occur [36]. However, SEP values of this study were smaller than SEC, which led to prevent the over fitting.

Fig. 3 shows data distribution of calibration and prediction of pH. The NIR calibration model with PLS algorithm was $y = 0.9927x + 0.0269$ with correlation coefficient (r) value was 0.9906. This r value indicates that PLS was an appropriate calibration technique to extract spectra variation relate to pH of mango fruits. Another measurement of model reliability was coefficient variance (CV) value. This study found CV value of calibration model and validation for pH was 0.97 % and 3.36 %, respectively. Since both CV values of calibration and validation were lower than 5%, calibration model resulted was a very reliable (Mlček et al., 2006). Bias value at set calibration of this study was -0.002. When evaluation was conducted using new sample at set validation, Bias value was 0.004. It showed that accuracy of calibration could be maintained to predict pH.

TABLE II
CALIBRATION AND VALIDATION OF NIR MODEL FOR pH

	Calibration		Validation	
Bias	-0.002	N	102	0.004
SEC	0.03	SEP		0.012
CV (%)	0.97	CV (%)		3.36
R ²	0.99	R ²		0.82

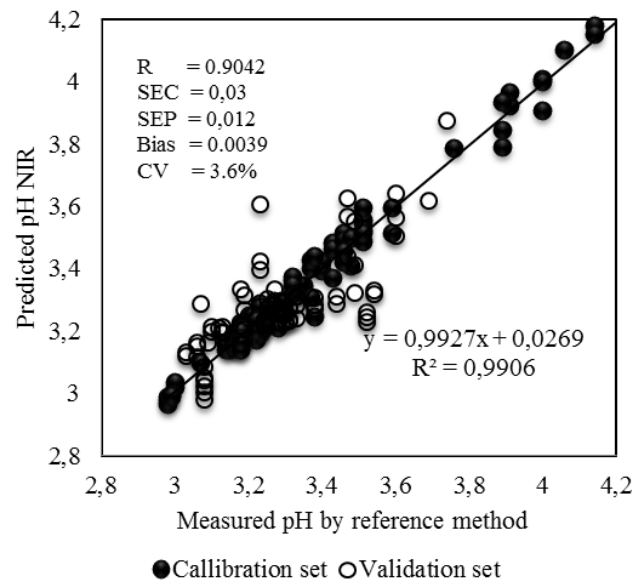


Fig. 3. Measured pH by reference method and predicted pH by NIR

IV. CONCLUSION

This study has established a technique, based on NIR spectroscopy of the fruit, for predicting the internal attribute parameters (pH) of mango fruits cv Gedong Gincu. By means of partial least square (PLS) regression relationship was established between reflectance spectra and pH parameter. PLS method seemed to produce the good calibration results for pH prediction. The predicted values were highly correlated with destructively measured values. The coefficient of correlation (r) of pH was 0.9042 and standard error of prediction (SEP) was 0.12 respectively. It was concluded that by using the NIR spectroscopy measurement system, in the appropriate spectral range, it is possible to nondestructively predict the pH of mango fruit. Further work may be carried out to develop calibration model and prediction more internal quality attributes of mango fruit.

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