THE APPLICATION OF NEAR INFRARED TECHNOLOGY AS A RAPID AND NON-DESTRUCTIVE METHOD TO DETERMINE VITAMIN C CONTENT OF INTACT MANGO FRUIT
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APLIKASI TEKNOLOGI SINAR INFRAMERAH SEBAGAI METODE CEPAT DAN TANPA MERUSAK UNTUK PREDIKSI KADAR VITAMIN C PADA BUAH MANGGA

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ABSTRACT
In the present study, we investigated the potential application of infrared technology based on near infrared reflectance spectroscopy (NIRS) as rapid, robust and non-destructive tool to determine vitamin C content of intact mango. Near infrared spectral data, in wavelength range from 1000 to 2500 nm were acquired for a total of 62 mango samples. Spectra data were enhanced using extended multiplicative scatter correction (EMSC) prior to prediction models development. Vitamin C content of intact mangoes was predicted using two different regression approaches namely principal component regression (PCR) and partial least square regression (PLSR). Prediction performances were justified using several statistical indicators namely correlation coefficient (r), root mean square error (RMSE), and residual predictive deviation (RPD) index. The results showed that vitamin C can be predicted using NIR technology with maximum r = 0.99, RMSE = 1.33 and RPD = 5.40. It may conclude that NIR technology can be applied as an alternative fast, robust and non-destructive method in determining vitamin C content of intact mango.

ABSTRAK
Studi ini bertujuan untuk mengkaji potensi teknologi sinar inframerah sebagai metode alternatif baru yang cepat dan tanpa merusak untuk prediksi kadar vitamin C pada buah mangga utuh. Data spektrum inframerah diakuisisi dalam bentuk pantulan semu dengan panjang gelombang 1000 – 2500 nm untuk total 62 sampel buah mangga. Kadar vitamin C diprediksi dengan membangun model regresi berbasis metode PCR dan PLSR. Akurasi dan kehandalan model prediksi dikuantifikasi dengan parameter statistik: koefisien korelasi (r), standar error (RMSE) dan indeks kehandalan (RPD). Hasil studi menunjukkan bahwa teknologi inframerah dapat memrediksi vitamin C buah mangga dengan akurasi r = 0.99, RMSE = 1.33 dan RPD = 5.40. Dapat disimpulkan bahwa teknologi NIRS dapat diterapkan sebagai metode alternatif xang cepat dan akurat untuk prediksi vitamin C pada buah mangga utuh.

INTRODUCTION
Mango (*Mangifera indica*. L) is one of the tropical fruits well known for the people around the world because of its benefits, source of vitamins and high nutritional value. Mangoes are cultivated and produced in many orchards with approximately 60% in more than 80 countries worldwide. Total production of mangoes was more than 43.5 million tons in 2017 (*Wendel et al., 2018*). They gain economic importance worldwide, which is gradually increased every year. Mango is consumed both as fresh fruit as well as in processed form. In most of the mango producing countries, most of mango fruits are consumed as fresh fruit (*Jha et al., 2012*).

Quality of mango fruit is mainly determined by various physiological parameters such as soluble solids content (SSC), vitamin C content, pH, dry matter, starch content and total acidity. Thus, quality evaluation plays important roles in agricultural and horticultural product industries. Most of the consumers require agricultural products, fruits and vegetables of good quality. They want to be sure that they are supplied with trusted and sealed good quality product since consumers are willing to pay high prices for them *(Munawar et al., 2016*).

Vitamin C is one of the most important quality parameters of fruits which have medical effects as antioxidant and help improving immune system in human body. To determine and measure Vitamin C or other chemical quality parameters of fruits, many methods have been widely used and applied. However, most of these conventional methods were based on standard laboratory analysis which required extraction of the fruit followed by complicated procedures *(Marques et al., 2016; Yusmanizar et al., 2019*). Especially for vitamin C, common titration method was generally used (*Munawar et al., 2013*). This analysis firstly started with fruit pulp taken followed by other liquid solution added during measurement. Since some chemical materials are used, this analysis has also the potential to cause environmental pollution and requires destructing the object. Thus, it is not suitable to be applied in agricultural and horticultural industries which require fast and real-time quality evaluation.

To overcome this matter, alternative methods were required to predict inner quality parameters of fruit and other agricultural products. These methods must be fast, with simple preparation, robust, non-destructive, environmental friendly and pollution free. Infrared technology based on near infrared reflectance spectroscopy (NIRS) has been investigated and widely employed in many sectors including in agriculture and animal sectors *(Devianti et al., 2019; Nordey et al., 2017; Samadi et al., 2018*). Numerous studies imply that NIRS system has been implemented to measure and determine various quality parameters which normally related to chemical properties of those products: SSC, vitamin C content, pH, protein content, carbohydrates and others.

Near infrared reflectance spectroscopy (NIRS) method, works based on the principle of interaction between electromagnetic radiation, which normally comes from the light source, and biological objects (*Pasquini, 2018*). When light goes through and penetrates the biological object, there are several interactions that happen instantly. Those interactions can be reflection, absorption or transmittance *(Arendse et al., 2018*). Each biological object has its own special optical properties and patterns, which means that it has a different spectrum indicated by its chemical composition. Therefore, it is considered to be potential and suitable to predict internal quality of food and agricultural products since this method is characterized by simple preparation procedure, it is fast (approximately not more than 60 seconds), robust and pollution free because there are no chemical materials used during analysis (Deng et al., 2018). Most important, the NIRS method can predict several quality parameters simultaneously and with the same spectra acquisition.

Based on the advantages and excellence of NIRS as novel and robust method to measure various agricultural products, we attempted to investigate the feasibility of near infrared spectroscopy (NIRS) method and apply it in predicting vitamin C content in intact mango samples. Prediction models were developed using original unenhanced raw basic spectrum and enhanced near infrared spectrum using extended multiplicative scatter correction (EMSC) method. We also studied the impact of this spectra enhancement method to the prediction accuracy and robustness.

MATERIALS AND METHODS

Mango samples

A total of 62 intact mangoes (cv. *Kent* and *Palmer*) were used as samples on this experiment with different maturity stages from unripe to over-ripe stage. Samples were purchased and obtained at local market auction in Göttingen and stored at 25^{o}C for two days to equilibrate their inner temperature before spectra acquisition and further chemical analysis.

Near infrared spectral data

Near infrared (NIR) spectra data of intact mango samples were acquired and recorded using Fourier transform infrared instrument (FTIR, Thermo Nicolet Antaris II MDS) as shown in Fig.1. The basic spectra measurement using Photodiode sensor was chosen for this acquisition. Near infrared spectra data was obtained in wavelength range from 1000 to 2500 nm. Resolution window was set to 0.2 nm and spectral data were recorded as diffuse reflectance (Log(1/R)) spectrum and stored in local computer *(Munawar et al., 2016*).

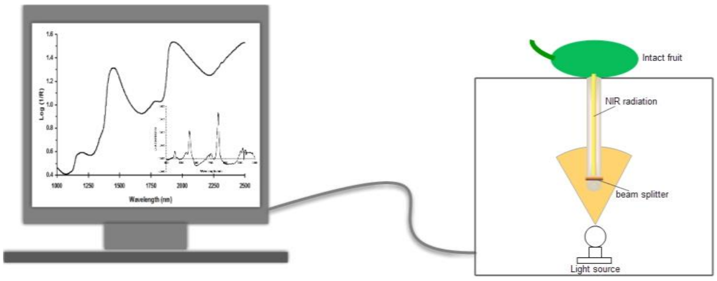

Fig. 1 – Near infrared spectra data acquisition for intact mango

Reference measurement of mango fruit vitamin C content

After acquiring and recording near infrared spectra data, all mango samples were further analysed for their inner quality parameters in the form of vitamin C. This analysis was conducted by making juice from 25 grams of mango pulp sample. Then, 100 ml of distilled water was added to the supernatant juice. Titration method was applied to measure vitamin C using 2.6 *Dichlorophenolindophenol* solution. The vitamin C content was then obtained by quantifying the reaction on the mixture solution which was indicated by colour changes from blue to light red. The averaged vitamin C analysis is expressed in mg.100g^{-1} fresh mass (FM) and measured in triplicate *(Subedi and Walsh, 2011*).

Near infrared spectra data enhancement

In order to achieve robust and accurate prediction models, near infrared spectra data were first analysed to inspect spectral visualization and noises recognition due to light scattering and interfered medium. These noises may disrupt desired relevant information related to chemical properties of mango samples. Therefore, it is very important to correct and enhance near infrared spectrum prior to calibration modelling. In this study, we employed extended multiplicative scatter correction (EMSC) method to enhance spectral data and investigated the impact of this correction method on the prediction performance.

Prediction model

Prediction models, used to predict vitamin C of intact mangoes, were developed simultaneously based on un-enhanced original spectra (raw spectrum) and enhanced spectra data (EMSC spectrum). Prediction models were established using two different regression approaches namely principal component regression (PCR) and partial least square regression (PLSR). The models were evaluated and validated using 10-fold cross validation method. Their accuracy and robustness on vitamin C prediction were then compared.

Prediction model performance

Prediction models performances were evaluated and judged for their accuracies and robustness using these following statistical indicators: the coefficient of determination (R^2), correlation coefficient (r), root mean square error (RMSE) and the residual predictive deviation (RPD) defined as the ratio between the standard deviation and the RMSE. Good and excellent prediction model performance should have high R^2, r coefficient (equal to or above 0.8), high RPD index (above 3) and low RMSE *(Cozzolino, 2014; Deng et al., 2018*).

$$RMSEC, RMSEP = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{y}_i - y_i)^2} \tag{1}$$

$$RPD = \frac{SD_{ref}}{RMSEP} \tag{2}$$

Where $\hat{y}_i$ is the predicted value of the *i-th* observation, y_i is the measured value of the *i-th* observation from desired quality attributes, n is the number of observations in the calibration, validation or prediction set, and *ym* is the mean value of the calibration or validation data set. The root mean square error prediction (RMSEP) is an estimate of total prediction error for an independent validation dataset.

RESULTS

Near infrared spectrum of intact mango

Diffuse near infrared reflectance spectrum, in wavelength range from 1000 to 2500 nm, after enhanced by EMSC method is shown in Fig. 2. This spectrum correction method enhanced spectral appearance and properties by normalizing spectrum to its ideal condition which is normally mean spectrum *(Devianti et al, 2019).* The chemical properties of those mango samples can be revealed based on this spectrum using special statistical methods namely chemometrics. Based on Figure 1, we may see that mango spectrum have shown clear pattern of C-H-O, N-H and O-H absorption bands in the near-infrared region whereas each chemical bond has a specific wavenumber and vibrational frequency from which quality parameters of mangoes like vitamin C can be predicted.

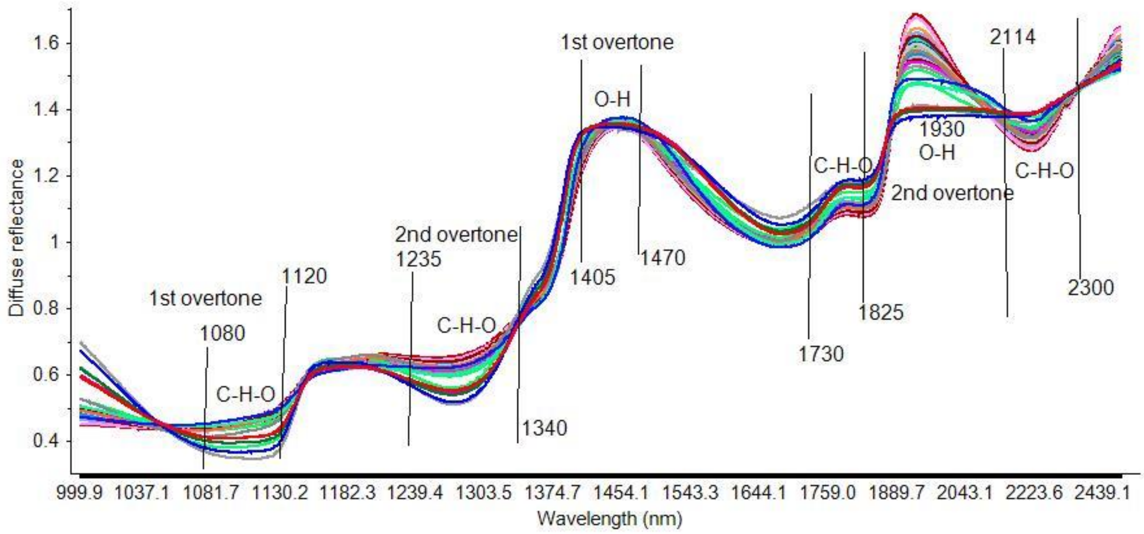

Fig. 2 - Near infrared spectrum of 62 intact mango fruits after correction using EMSC method

As we know that mango contains more than 85% water, the presence of water content can be observed in the wavelength range from 1405 to 1470 nm where O-H bonds were vibrated as 1st overtone on this wavelength range. Then, 2nd overtone of O-H bonds, which is correlated to water content of mango samples, was vibrated in wavelength 1930 nm. Similar findings were also noted in Nordey et al. (2017) where water content of fruit samples was vibrated in wavelength region of 1420 nm and 1940 nm. As shown in Fig.2, the highest peak was observed at wavelength 1490 nm and 1920 nm which were associated with O-H bands. Furthermore, vitamin C, which was constructed with C-H-O bonds, was vibrated in wavelength range around 2140 – 2255 nm, 2350 nm and 2390 nm. Thus, we may argue that Vitamin C of intact mangoes can be predicted in those wavelength regions. We also believe that besides vitamin C, soluble solids contents, individual sugars and total acidity of mango fruits can be determined as well in the wavelength regions mentioned.

Vitamin C content prediction models

The core part of near infrared spectroscopy technique develops and establishes calibration models used to predict quality attributes of organic and biological samples; in this study we investigated them on mango samples. The most accurate and robust models were then transferred onto NIR instrument for further quality evaluation. In this study, prediction models were developed using two different regression approaches namely principal component regression (PCR) and partial least square regression (PLSR). Prediction performances resulted from these two approaches were compared based on statistical indicators: correlation coefficient (r), root mean square error (RMSE) and residual predictive deviation (RPD) index.

First, vitamin C content prediction models were established using PCR regression approach where these models were constructed using both raw un-enhanced spectrum and enhanced EMSC spectrum. Prediction result for vitamin C content of 62 intact mango samples using PCR approach was shown in Table 1 and Fig.3. It can be seen from Table 1 that NIRS seems feasible to be used as rapid and non-destructive method; even using un-enhanced spectrum, the vitamin C content of intact mango can be predicted quite well with correlation coefficient of 0.86, RMSE = 6.71, RPD = 1.07 categorized as coarse prediction performance. When the model was constructed using enhanced EMSC spectrum, prediction accuracy and robustness slightly increased and improved. Correlation coefficient between predicted and actual vitamin C increased to 0.92 whilst RMSE is decreased to 5.26, and RPD index also increased to 1.36 categorized as sufficient prediction performance. Scatter plots derived from predicted and actual vitamin C content based on PCR regression approach were presented in Fig.3.

Table 1

Prediction performance using PCR regression approach

Spectrum	Statistical indicator			
	R^2	r	RMSE	RPD
Raw	0.74	0.86	6.71	1.07
EMSC	0.84	0.92	5.26	1.36

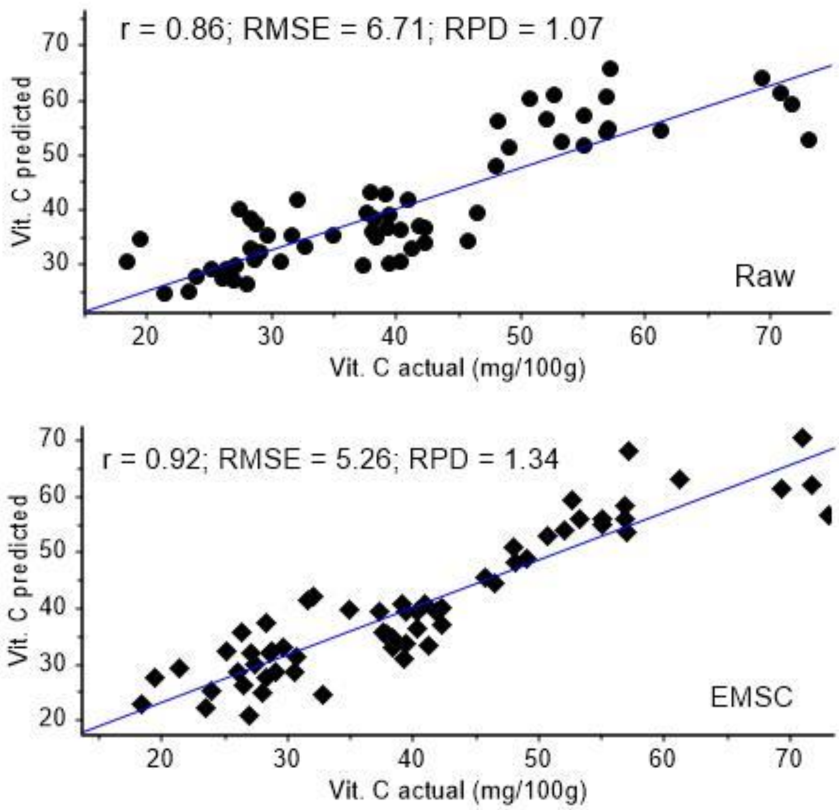

Fig. 3 - Scatter plot between actual and NIRS predicted vitamin C content of intact mangoes using PCR approach with un-enhanced (raw) and enhanced (EMSC) spectrum

Furthermore, prediction models were then constructed and developed using partial least square regression (PLSR) approach with un-enhanced raw spectrum and enhanced EMSC spectrum. Prediction result is shown in Table 2 and Fig. 4 where correlation coefficient r was better than PCR approach. The r coefficient of raw un-enhanced spectrum was 0.89 whilst RMSE was 6.03 and RPD index was 1.19 which was better than PCR approach.

From the spectrum point of view, it is obvious that enhanced spectrum using EMSC correction method, clearly and significantly improved prediction accuracy and robustness. The correlation coefficient was increased to 0.99, RPD index was also increased to 5.40 whilst RMSE decreased to 1.33, which is categorized as excellent and robust prediction performance. Based on literature *(Arendse et al., 2018; Comino et al., 2018)*, RPD between 1.0 – 1.5 means that prediction performance was still coarse and require some improvements especially on spectral data correction. Then, RPD value between 1.5 and 2.5 indicates that prediction performance is categorized as sufficient performance. Moreover, RPD value between 2.5 and 3 is categorized as good prediction whilst RPD above 3 indicates excellent accuracy prediction performance. Scatter plots derived from predicted and actual vitamin C based on PLSR regression approach were presented in Fig.4.

Table 2

Prediction performance using PLSR regression approach

Spectrum	Statistical indicator			
	R^2	r	RMSE	RPD
Raw	0.74	0.86	6.71	1.07
EMSC	0.84	0.92	5.26	1.36

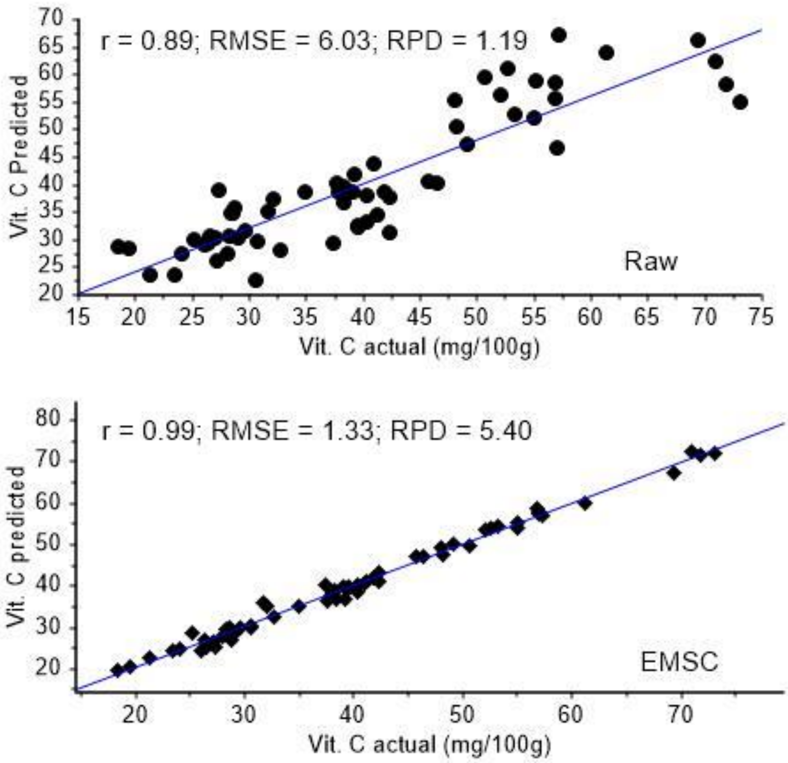

Fig. 4 - Scatter plot between actual and NIRS predicted vitamin C content of intact mangoes using PLSR approach with un-enhanced raw and enhanced EMSC spectrum

In general, judging from prediction performances, it seems that near infrared spectroscopy (NIRS) can predict vitamin C content of intact mango with maximum correlation coefficient of 0.99 and RPD index 5.40. NIRS can be used and improved by correcting and enhancing spectra data and in this study we used extended multiplicative scatter correction (EMSC). The achieved RPD maximum was 5.40, indicating excellent prediction performance. Further study might be continued to apply and employ NIRS method to predict other quality parameters of mangoes such as total acidity, soluble solids content, fibre content, pH, individual sugars (maltose, glucose) and firmness. We strongly believe that infrared technology based on NIRS can be used and applied as an alternative fast and robust method to predict inner quality parameters of mangoes and other agricultural products.

CONCLUSIONS

Based on our obtained experiments, we may conclude that near infrared spectroscopy (NIRS) can be applied as an alternative fast, non-destructive and robust method used to predict vitamin C content of intact mangoes. Spectra correction using extended multiplicative scatter correction (EMSC) was significantly improved and increased prediction accuracy and robustness. Thus, it can be inferred that infrared technology based on NIRS is potential and feasible to be used as fast, robust and non-destructive method in predicting vitamin C content and also other chemical quality parameters of intact mango fruits.

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