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Classification of N, P, and K concentrations in durian (*Durio Zibethinus* Murray CV. Mon Thong) leaves using near-infrared spectroscopy

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Abstract

A good durian fruit should be supported by sufficient nutrient concentrations. If farmers can quickly determine the nutrient concentration in leaves, they can control fertilisation. Near-infrared (NIR) spectroscopy is a rapid non-destructive test for estimating nutrient concentration. Measuring nutrient concentrations requires chemical analysis and is a time-consuming process. The aim of this paper is a preliminary test for classifying the N, P, and K concentration levels to determine the possibility of creating models in the future to help farmers obtain information on durian tree nutrient requirements quickly. The models reported in this paper were created by PLS-DA, which had higher accuracy than SVM and the SIMCA method. Fresh durian leaf samples were used, and the spectra provided greater accuracy than the dried ground leaf sample spectra. The classification models had an accuracy of 88.89, 81.25, and 86.36% for predicting N, P, and K, respectively.

Keywords: Durian leaf, Near-infrared spectroscopy, Nitrogen, Phosphorus, Potassium

1. Introduction

In plants, leaves are the main component that produce food by photosynthesis [1]. The macronutrients comprise nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulphur (S) [2]. N is a major factor in photosynthesis [3] and comprises the chlorophyll in leaves [4]. P is important for controlling plant growth [5], and K plays an important role in many physiological functions for plant growth [6]. These nutrients are essential for the growth and productivity of plants. If a durian tree lacks a nutrient (N, P, and K) in each growth stage, there will be an impact on the product. In durian planting, a tree will need more nutrients at different stages. To start planting one to five years before fruit production, a tree needs more N [7] because N supports plant health, growth, and photosynthesis [8]. After plant flowering, it needs more P and K [7] because P helps produce many flowers and K helps strengthen the flowers [9]. In fruit setting and fruiting, the tree needs more K [7] because K enhances the quality of young fruit [9]. After harvesting, the tree again needs more N [7] to prepare for the next season.

In the near-infrared (NIR) spectroscopy field, research has been done on leaves to predict nutrients. Galvez-Sola et al. [10] reported using NIR spectroscopy for predicting N in dried citrus leaves, obtaining an R value of 0.99. Menesatti et al. [11] used NIR spectroscopy to predict N and K in fresh orange leaves, reporting R values of 0.909 and 0.991, respectively. Yarce and Rojas [12] used NIR spectroscopy to predict P and K in dried sugarcane leaves, obtaining R values of 0.988 and 0.979, respectively. Chen et al. [13] used NIR spectroscopy to predict P in fresh sugarcane leaves (R=0.68).

This research focuses on the preliminary study of using NIR spectroscopy with durian leaves to classify nutrient levels. In the traditional method for N, P, and K nutrient analysis, ICP-OES and TruMac CNS analyses can be used; however, these methods require approximately one week to obtain the data, as after a sample of the dried ground leaf is obtained, the sample needs to be digested in liquid nitrogen before being analysed by ICP-OE. If farmers can estimate the nutrient content in leaves at each growth stage, they can save time and control fertilising to reduce costs, increase profits, obtain quality fruit, and protect the environment. As a result, Thailand can reduce the import of fertilisers and increase exports.

2. Materials and methods

2.1 Samples

The fresh leaves of durian (*Durio zibethinus* Murray CV. Mon Thong [14]) were collected from Rayong, Chanthaburi, and Trad in Thailand. The samples were fresh leaves and dried ground leaves. For dried ground leaves, one sample of 20 fresh leaves was collected

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from one durian tree. After collecting fresh leaf samples, the samples were washed with 0.1 N HCl acid and rinsed three times with distilled water. Subsequently, samples were dried at 70°C for 48 h, crushed, and sieved through 40 mesh (0.42 mm) perforated screen [15]. Samples were obtained over one year (December 2019 to November 2020) to capture the various levels of nutrients at different durian tree growth stages. In nitrogen (N) classification, a total of 36 samples were used (3 concentration and 12 samples from each concentration). For phosphorous (P) classification, 48 samples were used (3 concentrations and 16 samples for each concentration). Potassium (K) classification used 66 samples (2 concentrations and 33 samples for each concentration).

2.2 NIR Scanning

The fresh leaves on the tree sample were scanned (one average spectrum contained 20 fresh leaves. The sampled fresh leaves were old, dark green, and in the 2nd to 3rd leaf position from the tip of the branch. Each leaf was scanned in two positions (proximal and distal side) by a Micro-NIR spectrometer (Viavi, USA) in the wavelength range of 950-1,600 nm with reflectance mode, and while scanning, an aluminium plate for reflectance was placed under the leaf sample. After that, those samples were transported to the laboratory and scanned in the same way as on the durian trees by a Micro-NIR spectrometer and FT (Fourier transformed)-NIR spectrometer (Bruker Ltd., Germany) at a wavelength of 12,500-4,000 cm^{-1} (800-2,500 nm). The dried ground leaf sample was scanned using Micro-NIR and FT-NIR spectrometers with a quartz cup (4.3 cm diameter, 7.0 cm in height) [15].

2.3 Sample analysis

The dried ground leaf samples were analysed by TruMac CNS (Leco, USA) for nitrogen (N) and ICP-OES (Perkin Elmer, USA) for phosphorus (P) and potassium (K).

2.4 NIR Classification model and performance

Figure 1 showed schematic diagram of modeling process. The NIR classification model for predicting sufficient macronutrients was created by soft independent modelling by class analogy (SIMCA), support vector machine (SVM), and partial least squares-discriminant analysis (PLS-DA). SIMCA modelling requires a PCA model for each class to distinguish between members and non-members of the different classes [16]. SVM can be separated or classified using a separating hyperplane. The hyperplane was calculated using the following formula [17]:

$$y = w^T x + b \tag{1}$$

where w is support vector; b is constant

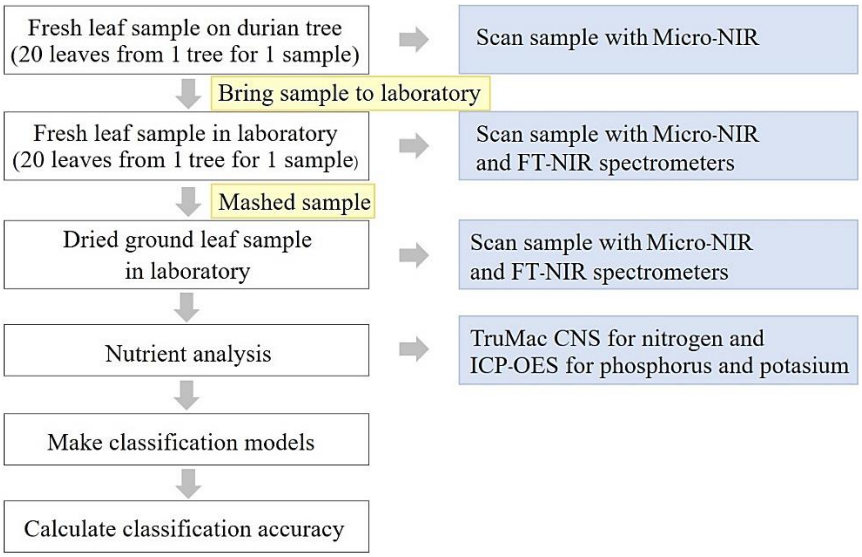

Figure 1 Schematic diagram of leaf sample analysis for plant nutrition in the field by Micro-NIR and in the laboratory by both Micro-NIR and FT-NIR spectrometers. Dried ground samples were analyzed by Micro-NIR and FT-NIR spectrometers and by traditional methods by TruMac CNS for nitrogen and ICP-OES for phosphorus and potassium. The classification model was made and the model accuracy was calculated.

PLS-DA is a classification method based on modelling the differences between several classes with PLS. The PLS model uses one response variable, which codes for class membership as follows: -1 for members of one class, +1 for members of the other one. The PLS model equation can be seen below [16]:

$$X = TP^T + E \tag{2}$$

$$y = Tq^T + f \tag{3}$$

where T is matrix of latent variables; P is X-loading
q is y-loading; E, f are constants

The software used for spectral and modelling analysis was OPUS v. 7.0.129 (Bruker Ltd., Germany) and The Unscrambler X 10.4 (Camo, Norway).

The accuracy of prediction models that were created with different methods was compared. The accuracy was calculated using the following formula [18]:

$$\text{Accuracy } (\%) = \frac{\text{Number of sample classified correctly}}{\text{Total number of sample}} \times 100 \quad (4)$$

3. Results

Table 1 shows the nutrient concentrations in leaves at sufficient levels for the growth of durian trees. The leaf samples at the 2nd to 3rd leaf position of the lateral shoot tip were collected. Sufficient concentrations of N, P, and K in the leaves of durian trees should have an approximate value of 2.00-2.30, 0.15-0.25, and 1.70-2.50%, respectively [19]. Thus, the nutrient concentration levels were divided into three levels: less than sufficient, sufficient, and more than sufficient, but for our samples, the K concentration had two levels because the soil in the eastern part of Thailand was highly acidic, the texture was coarse, and there was heavy rain, which caused the loss of potassium [20].

Table 1 Nutrient concentrations in leaves for the growth of durian trees [19].

Nutrient	Nutrient concentration (%)		
	Less than sufficient	Sufficient	More than sufficient
N	< 2.00	2.00-2.30	> 2.30
P	< 0.15	0.15-0.25	> 0.25
K	< 1.70	1.70-2.50	-

The model created by PLS-DA had a higher accuracy than those models created by SVM and SIMCA (data not shown). Table 2 shows the accuracy of the nutrient concentration classification models by PLS-DA using Unscrambler X 10.4 software. All models used raw spectra and full wavelengths except the fresh leaves on the tree spectra; the wavelengths were cut at 908.1-1, 124.9 nm because the wavelengths were abnormal due to unstable temperatures and light while scanning. For N, the model made from the dried ground leaf sample scanned with a Micro-NIR spectrometer had an accuracy of 86.11%, and the model made from the fresh leaf sample scanned with an FT-NIR spectrometer had an accuracy of 83.33%. For P, the model scanned using an FT-NIR spectrometer had an accuracy of 64.58% for the dried ground leaf samples and 62.50% for the fresh leaves. For K, the model made from the dried ground leaf sample scanned using a Micro-NIR spectrometer had an accuracy of 80.03%, and the model scanned with an FT-NIR spectrometer had an accuracy of 84.85% for both fresh leaves and dried ground leaf samples.

Table 3 shows the performance of the classification models in predicting nutrient concentrations using OPUS v. 7.0.129 software. The models used pre-treated and selected wavelengths. The models that used the fresh leaf samples had higher accuracy than those of the dried ground leaf samples. The accuracy of the models obtained from the fresh leaf sample was 84.85, 81.25, and 86.36% for classifying N, P, and K, respectively.

Table 2 Performance of the classification models in predicting nutrient concentrations using Unscrambler X 10.4 software.

Nutrient	Sample	Spectrometer	Wavelength (nm)	Rank	Accuracy (%)
N	fresh leaves on tree	Micro-NIR	1124.9-1676.2	7	50.00
	fresh leaves in laboratory	Micro-NIR	908.1-1676.2	7	63.83
		FT-NIR	800.7-2782.4	7	83.33
	dried ground leaves in laboratory	Micro-NIR	908.1-1676.2	7	86.11
		FT-NIR	800.7-2782.4	7	61.11
P	fresh leaves on tree	Micro-NIR	1124.9-1676.2	7	35.42
	fresh leaves in laboratory	Micro-NIR	908.1-1676.2	7	52.08
		FT-NIR	800.7-2782.4	7	62.50
	dried ground leaves in laboratory	Micro-NIR	908.1-1676.2	7	41.67
		FT-NIR	800.7-2782.4	7	64.58
K	fresh leaves on tree	Micro-NIR	1124.9-1676.2	7	51.51
	fresh leaves in laboratory	Micro-NIR	908.1-1676.2	7	74.24
		FT-NIR	800.7-2782.4	7	80.03
	dried ground leaves in laboratory	Micro-NIR	908.1-1676.2	7	84.85
		FT-NIR	800.7-2782.4	7	84.85

Table 3 Performance of the classification models in predicting nutrient concentrations using OPUS v. 7.0.129 software.

Nutrient	Sample	Wavenumber (cm^{-1})	Wavelength (nm)	Pre-Treatment	Rank	Accuracy (%)
N	fresh leaves in laboratory	9403.8-6094.3 5454.0-4597.7	1063-1641 1834-2175	first derivative + straight-line subtraction	7	88.89
	dried ground leaves in laboratory	9403.8-7498.3	1063-1334	first derivative + straight-line subtraction	3	80.56
P	fresh leaves in laboratory	9403.8-7498.3 6102.0-5446.3	1063-1334 1639-1836	first derivative + straight-line subtraction	7	81.25
	dried ground leaves in laboratory	9403.8-4242.9	1063-2357	MSC	1	58.33
K	fresh leaves in laboratory	7506.0-6094.3 5454.0-4242.9	1332-1641 1834-2357	raw spectra	4	86.36
	dried ground leaves in laboratory	6102.0-5446.3 4605.4-4242.9	1639-1836 2171-2357	min-max normalisation	6	86.33

The PLS-DA model created from fresh leaf samples had a higher R^2 value, thus achieving a higher accuracy of classification than the model created from dried ground leaves. The fresh leaf model for classification of N and K selected a peak of water (1450 and 1940 nm) to create the model, indicating that the moisture content in the leaf influenced model prediction, but the dried ground leaf contained too little moisture.

The classification made with pre-treatment and selected wavelength had an accuracy higher than the model made with raw spectra and full wavelengths. The best models for predicting nutrient concentrations were focused. The best models for predicting N, P, and K concentrations were obtained using the fresh leaf samples with pre-treatment and selected wavelengths. The model of N used a wavelength of 1,063-1,641 and 1,834-2,175 nm and was pre-treated by first derivative + straight-line subtraction. The model of P used a wavelength of 1,063-1,334 and 1,639-1,836 nm and was pre-treated by first derivative + straight-line subtraction. The model of K used wavelengths of 1,332-1,641 and 1,834-2,357 nm and used no pre-treatment.

Figure 2 shows the raw spectrum of durian leaves and the X-loading weight plot of the classification model for predicting nutrient (N, P, and K) concentrations (Figure 3). The regression coefficient plot of the classification model for predicting nutrient (N, P, and K) concentrations is represented in Figure 4. Table 4 shows the absorption bands with high regression coefficients of the classification model in predicting nutrient concentrations. The regression coefficient of N had high bands at 1,403, 1,876, 1,994, and 2,035 nm. The wave band at 1,395 nm was related to CH_2 [21], 1,900 and 2,000 nm was related to starch, and 2,050 nm was related to protein [19]. For P, high bands were at 1,064, 1,088, 1,098, and 1,147 nm. The wave band at 1,053 nm was related to CH_2 [21], 1,080 nm was related to benzene [21], and 1,152 nm was related to CH_3 [21]. For K, the high bands were at 1,754, 1,773, and 1,800 nm. The wave band at 1,765 nm was related to CH_2 [21] and 1,780 and 1,820 nm were related to cellulose [21].

Rotbart et al. [22] estimated the olive leaf nitrogen concentration using visible and NIR spectral reflectance and found that NIR could be applied to classify N concentrations in olive leaves using a Luminar-5030 spectrometer (1100-2500 nm) and reported an accuracy of 83%. That research suggested a model with dried ground leaf samples and a spectral range of 1,100-1,700 nm, which was different from this study. In this research, the model from fresh leaves was more accurate than that for dried ground leaves. The fresh leaf model for the classification of N selected a peak of water (1450 and 1940 nm) to create the model, indicating that the moisture content in the leaf influenced model prediction.

However, to the best of our knowledge, the classification of P and K concentration levels has not been reported.

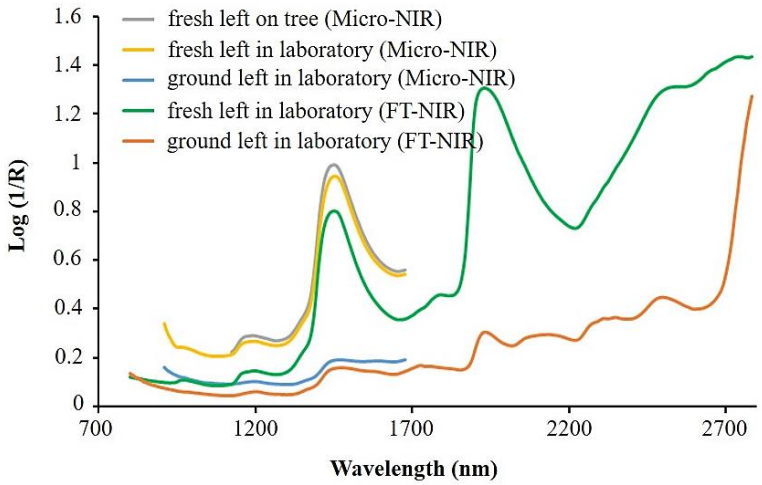

Figure 2 Raw spectrum of durian leaves

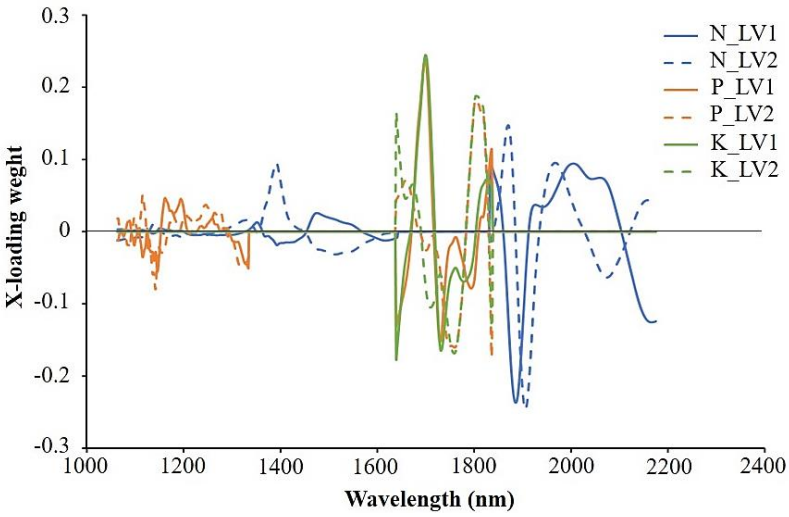

Figure 3 X-Loading weight plot of the classification model for predicting nutrient (N, P, and K) concentrations

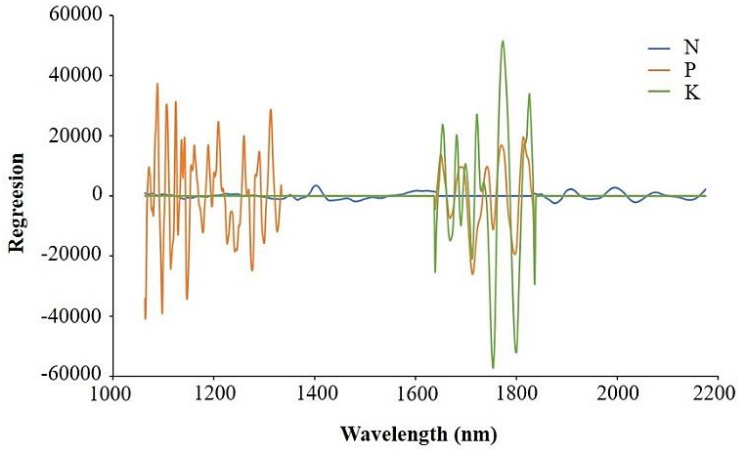

Figure 4 Regression coefficient plot of the classification model for predicting nutrient (N, P, and K) concentrations

Table 4 Absorption bands with high regression coefficients of the classification model for predicting nutrient concentrations [21]

Nutrient	Wavelength (nm)	Wavelength (nm) referred form reference	Bond vibration	Structure
N	1,403	1,395	2 x C-H str. + C-H def.	CH_2
	1,876	1,900	O-H str. + 2 x C-H str.	starch
	1,994	2,000	2 x C-H def. + C-O def.	starch
	2,035	2,050	N-H asym. Str. + amide II	protein
P	1,064	1,053	2 x C-H str. + 2 x C-H def. + $(CH_2)n$	CH_2
	1,088	1,080	2 x C-H str. + 2 x C-C str.	benzene
	1,098	1,080	2 x C-H str. + 2 x C-C str.	benzene
	1,147	1,152	C-H str. second overtone	CH_3
K	1,754	1,765	C-H str. first overtone	CH_2
	1,773	1,780	O-H str. + 2 x C-O str.	cellulose
	1,800	1,820	O-H str. + 2 x C-H str.	cellulose

4. Discussion

This paper is a report of a preliminary test on the classification of N, P, and K concentrations using NIR spectroscopy. The model made by PLS-DA had higher accuracy than those of other modelling methods. The PLS method reduced the number of variables, which also reduced the variance or the risk of overfitting [23].

For the models created by PLS-DA using OPUS software, the model selected a wavelength that was more accurate than the model using all wavelengths. Because the model should be created by a wavelength correlated with the predicted value, removing some wavelengths reduced noise [24]. To remove other interfering variables [25], spectral pre-treatment also improved the model's accuracy. The first derivative and straight-line subtraction methods reduced the problem of baseline shift [26].

The important structures correlated with the model of predicting levels of N was CH_2, starch, and protein. For P, CH_2, CH_3, and benzene were the structures correlated with the model. For K, the important structures were CH_2 and cellulose.

CH_2 is a component of chlorophyll [27] and glucose [28]. Starch, a carbohydrate, and protein are components of the cell wall. The cell wall was made up of about 90% carbohydrates and 10% protein [28]. Cellulose is also a component of the cell wall [28]. In plants, chlorophyll is used in photosynthesis to produce carbohydrates. CH_3 is one of the chemical bonds of chlorophyll [27]. Benzene comprised coumarins found in durian leaves [29].

This research demonstrated that it is possible to apply NIR spectroscopy to classify the concentrations of N, P, and K in durian leaves. However, additional samples should be collected to ensure that the model covers more characteristic variation.

5. Conclusions

According to this research, the best model was created by PLS-DA using fresh leaf samples and selected wavelengths. The classification model for predicting nutrient concentrations had an accuracy of 88.89, 81.25, and 86.36% for predicting N, P, and K, respectively. This shows the possibility for the development of classifying models. In the future, additional samples should be collected so that the model covers all concentrations. This model will enable farmers to predict nutrient concentrations in durian leaves and adjust fertilising according to each growth stage.

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