

Classification Technique for Using Near Infrared Spectroscopy to Detect Dry Juice Sac of Mandarin Fruit cv. Sai Nam Pueng

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Abstract

The use of chemometrics to analyze NIRs spectral data of Mandarin fruit *Citrus reticulata* cv. Sai Nam Pueng for dry juice sac detection was investigated. The total of 200 fruits (75 normal and 125 abnormal fruits) were acquired the spectral data using NIRSystem 6500 with fiber optic probe in the wavelength region from 700–1100 nm prior to determine the reference laboratory data including moisture content (MC), total soluble solid (TSS) and titratable acidity (TA). Then, the principal component analysis (PCA) and multiple linear regression - discriminant analysis (MLR-DA) were used to classify fruit with this symptom. It was found that Savitzky-Golay smoothing (10 nm average for left and right sides) and second derivative (10 nm average for left and right sides) were used as spectra pre-treatment method for the optimal PCA and MLR-DA model performances of MC, TSS and TA. The effective wavelengths in MLR-DA were at 826, 924, 962, 978, 1008 and 1028 nm. The precision of MLR-DA was 96%. There were only 4% of un-classify samples which were 1–25% of dry juice sac fruits and normal fruits. Therefore, MLR-DA could be the efficient method to classify a dry juice sac of Mandarin using non-destructive technique NIRs.

Keywords: Mandarin, Chemometrics, NIRs, Dry juice sac, PCA

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Received: 16 August 2018/ Revised: 15 November 2018/ Accepted: 3 March 2019

1. Introduction

Mandarin cv. Sai Nam Pueng is a tropical fruit which can be grown in both tropical and warm climates. They are popular in both characteristics of fresh fruit and juice. Because it has a high nutritional value. Over 5 years ago, the price of Mandarin orange has risen because the orange plantation area was greatly reduced. Original orange plantation areas such as Rangsit in Pathum Thani Province has decreased due to the expansion of the city. Mandarin orange plantation areas in the northern of Thailand have faced disease problems such as citrus greening disease, which resulted in orange trees deteriorate and gradually die. Currently, Mandarin orange leaved from the garden are priced from 34 to 40 baht per kilogram. One of the important problems of Mandarin cv. Sai Nam Pueng is a dry juice sac, which is found in the early and late season of productions for many reasons. Dry juice sac is not visible from the outside of fruit. Currently dry juice sac detection has been done only by the high skilled person. This is a limitation in the separating of dry juice sac fruit from the normal one. The mandarin is dry with thicker cell wall than normal fruit. The nutritional values, total soluble solid (TSS), titratable acidity (TA) and vitamin C decreased when it was compared to normal fruit while many minerals increase, especially Ca and Mg (Erickson, 1968). These physical and chemical properties are measured. Near-infrared Spectroscopy (NIRs) have been widely applied to assess the quality of agricultural products, such as the prediction of TA values in nectarines (Slaughter, 1996), TSS values in Sutsuma (Kawano *et al.*, 1993) and using NIR for detection of dry juice sac in Mandarin fruit by moisture content (Wongzeewasakun *et al.*, 2017). Therefore, objective of this research is to determine the relationship between the physical and chemical properties and dry juice sac. Using principal component analysis (PCA) and following by multiple linear regression - discriminant analysis (MLR-DA) to detect dry juice sac fruits from regular appearance. This will be a non-destructive, accurate, time-saving and chemical-required to measure chemical properties of Mandarin fruit.

2. Materials and Methods

2.1 Spectral acquisition

Two hundred samples of Mandarin fruit cv. Sai Nam Pueng were measured the spectral with Near Infrared Spectrophotometer. NIR spectrum of Mandarin fruits was measured in short wavelength region from 700–1100 nm (14,285–9,090 cm^{-1}) at harvest date with NIRsystem 6500 spectrophotometer (Foss NIRSystem, Silver Spring, USA). The NIRsystems 6500, all spectra were acquired raw spectrum using interactance mode with the fiber optic probe. To control the temperature of the samples at 25 °C, a water bath (EYELA, Japan) covered with thin polyethylene film. It was used for controlling the samples temperature by

dipping in 10 min before acquisition and throughout the experiment, room temperature has been controlled at 25 °C. The sample fruits were measured for NIR spectrum by averaging 50 scans. A reference measurement of Teflon cylinder was performed every 5 samples. Spectral data were recorded at cheek positions of Mandarin fruit, then peeled the Mandarin fruits to assess the degree of dry juice sac (Figure 1.). Then, sample fruits were measured level of dry juice sac area. It was divided into five score levels: normal fruit: 0; 1–25% of dry juice sac area: 1; 26–50% of dry juice sac area: 2; 51–75% of dry juice sac area: 3; more than 76% of dry juice sac area: 4. Then, studies the position of dry juice sac began from stem, cheeks and bottom of fruit.



Figure 1 Normal fruit (A) and dry juice sac fruit (B) of Mandarin fruit cv. Sai Nam Pueng

2.2. Physical and chemical property measurement

Mandarin fruit cv. Sai Nam Pueng for 200 samples were measured the physical and chemical properties of each moisture content (MC), total soluble solids (TSS) and titratable acidity (TA), then the relationship between degree of dry juice sac, physical and chemical properties were analyzed. Statistical analysis of measurements was carried out using SPSS. The experiment was analyzed by a Completely Randomized Design (CRD) in SPSS version 16. Data were subjected to analysis of variance (ANOVA) and Duncan Multiple Range Test ($p = 0.05$) calculated for the comparison of means.

2.3 Data analyses

Two methods were used for classification. First, used principal component analysis, PCA). It is a technique used for identification of a smaller number of uncorrelated variables known as principal components from a larger set of data. PCA is a tool used in predictive models and exploratory data analysis. Second, multiple linear regression - discriminant analysis (MLR-DA) was applied. The objective of this method is to establish a model one quantitative variable as a linear combination of others variables. The purpose of discriminant analysis is to obtain a model to predict a single qualitative variable from one or more independent variable(s). Both methods were used to separate dry juice sac Mandarin fruit from the normal fruit by using the Unscrambler ® version 9.8 (Camo, Oslo, Norway).

3. Results and Discussion

3.1 NIR spectra of each level of dry juice sac

The results of the study 2.1 were studied on the normal fruit and symptoms of dry juice sac fruit by using 100 dry Mandarins juice sacs. The results showed that dry juice sac started from stem for 82%, started from cheek for 14% and started from the bottom for 4%. Similar to Nakajima (1976) reported dry juice sacs of *Citrus tamurana* began to appear near the central axis and then spread along the side membranes of the segment. It was found that the epidermal cells of affected vesicles were twisted and dried out, showing comparatively high permeability of membranes to water. Moreover, some research found that dry juice sac was mostly found on flesh around the stem and expanded to other areas. Fruit with dry juice sac contained lower values of moisture content (MC), total soluble solids (TSS) and titratable acidity (TA) than normal fruit (Wongzeewasakun, 2017).

Figure 2 exhibits the mean original spectra of Mandarin fruit c.v. Sai Nam Pueng from interactance mode which shows a clear peak at 986 nm which is related to the second overtone of water. Normally, peak of water molecules showed a clear peak at 980 nm (Osborne, 1986), 964 nm (Kawano *et al.*, 1995) and 975 nm (Muenmanee *et al.*, 2016). The absorbance of water molecules in Mandarin fruit decreased when dry juice sac increased. It involves the expression of dry juice sac at each level.

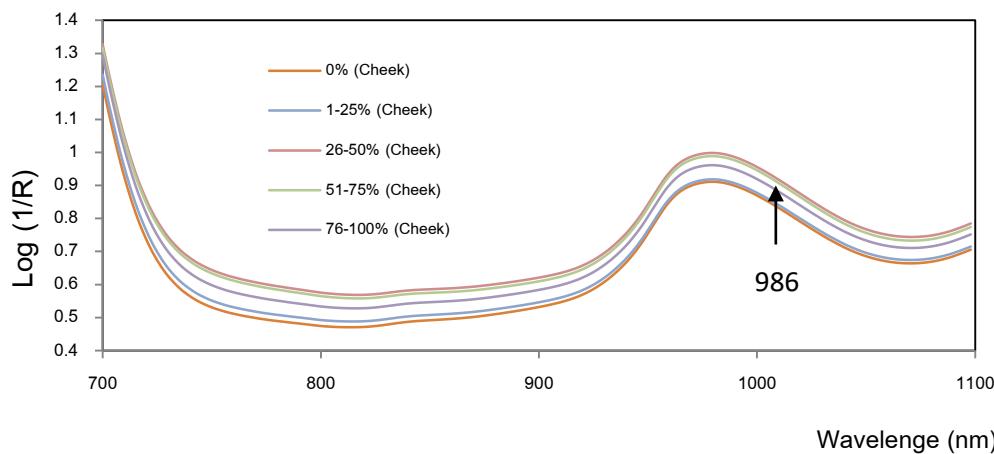


Figure 2 Original spectrum of normal and dry juice sac of Mandarin fruit at each symptom of dry juice sac level.

3.2 Physical and chemical properties

The results of the study 2.2. found that some parameters of MC, TSS and TA of between normal fruits and dry juice sac fruits at different levels were significantly different (Table 1). The result showed that the moisture content of normal fruit was $90.73 \pm 2.06\%$ wb which was greater than dry juice sac fruit, $(89.03 \pm 1.47) - (84.45 \pm 1.42)\%$ wb. MC clearly illustrates the decrease tendency of moisture content along dry juice sac development. Similar to TSS and TA were decreased, while level of dry juice sac of Mandarin increased.

Table 1. Physical and chemical properties of normal and dry juice sacs from Mandarin fruit

Dry juice sac level	MC (%)	TSS (%)	TA (%)
0	90.73 ± 2.06 a	11.99 ± 0.96 a	0.45 ± 0.07 a
1	89.03 ± 1.47 b	11.08 ± 1.59 b	0.36 ± 0.10 b
2	88.35 ± 1.64 b	10.94 ± 0.96 b	0.29 ± 0.08 c
3	85.96 ± 2.28 c	8.66 ± 1.70 c	0.25 ± 0.07 c
4	84.45 ± 1.42 d	8.94 ± 1.25 c	0.22 ± 0.06 c
CV (%)	3.30	16.61	33.54

Note: Table displays the values of mean \pm standard deviation (SD.)

In each column, different letters represent significant differences ($p \leq 0.05$) using Duncan Multiple Range's Test

3.3 NIR spectra of Mandarin fruit

From the spectrum there was absorption band at a wavelength of 962 nm, which is the water absorption band (Figure 3) as well as its research (Saranwong *et al.*, 2003). Gomez *et al.* (2006) reported that water peaks were found at a wavelength of 975 nm on the Sutsuma Spectrum. Moreover, Normally, peak of water molecules shows a clear peak at 980 nm (Osborne, 1986), 964 nm (Kawano *et al.*, 1995), 975 nm (Muenmanee *et al.*, 2016) and 976 nm (Jannok *et al.*, 2014). The moisture content in juice sacs was affected to NIR spectra. Low moisture content in dry juice sac fruit showed the lower NIR absorbance than high moisture content in normal fruits. However, percentage of dry area of juice sac (1–25%) was the same level as normal fruit when detected by NIR.

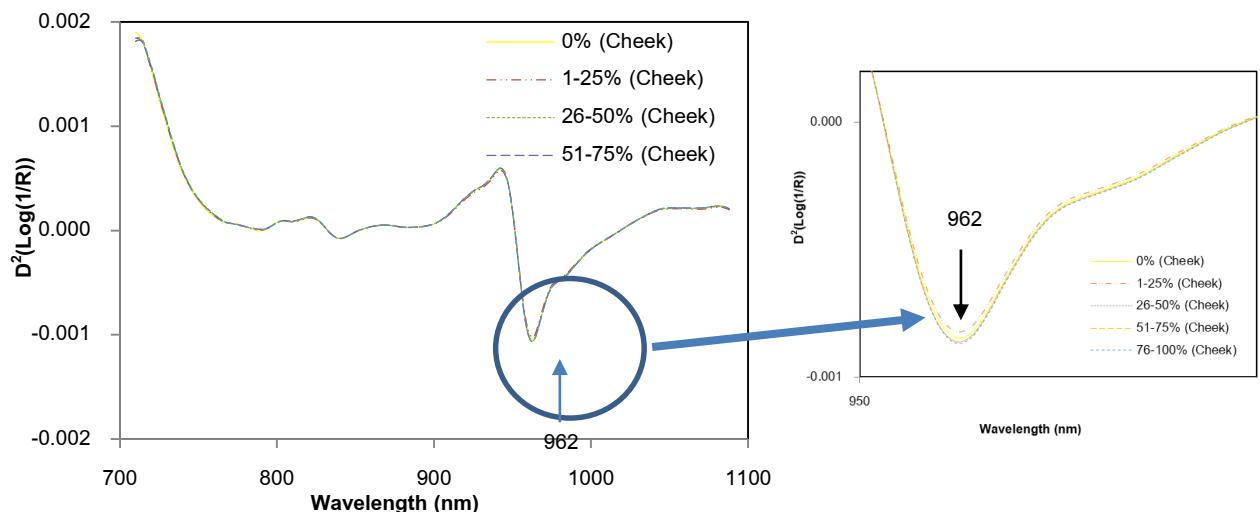


Figure 3 Second derivative spectra of cheek position Mandarin fruit having normal fruit, dry juice sac 1–25%, dry juice sac 26–50%, dry juice sac 51–75% and dry juice sac more than 76%

3.4 Dry juice sac classification

Analyses using PCA can be used to detect dry juice sac Mandarin fruit only 51% because some of less level of dry juice sac Mandarin fruit were in the same group of normal Mandarin fruits. (Figure 4).

Then, analyses data using multiple linear regression and discriminant analysis (MLR-DA) were used to classify this symptom. It was found that Savitzky-Golay smoothing (10 nm average for left and right sides) was used as spectra pre-treatment method for the optimal MLR-DA model performance of MC, TSS and TA. The effective wavelengths in MLR-DA were at 826, 924, 962, 978, 1008, 1028 nm (water and sugar peak) as shown in (Table 2). As well as its research Williams and Norris (1998) reported that water peaks were found at the wavelengths of 938, 958, 978, 986, 1010 and 1030 nm sugar peaks were found at the wavelength of 838, 888, 913 and 1005 nm. The classification accuracy of MLR-DA was 96%. There were only 4% of un-classify samples which were 1–25% of dry juice sac fruits and normal. In addition, Timkhun *et al.* (2013) reported that the discriminant analysis can be predicted dry juice sac by firmness cheek with 75 percent accuracy. In the verification experiment, 200 tangerines purchased from Nan market were classified with 80.8 percent accuracy using cheek firmness by using NIRs.

Therefore, MLR-DA could be the efficient method to classify the dry juice sac symptom of Mandarin using non-destructive technique, NIRs.

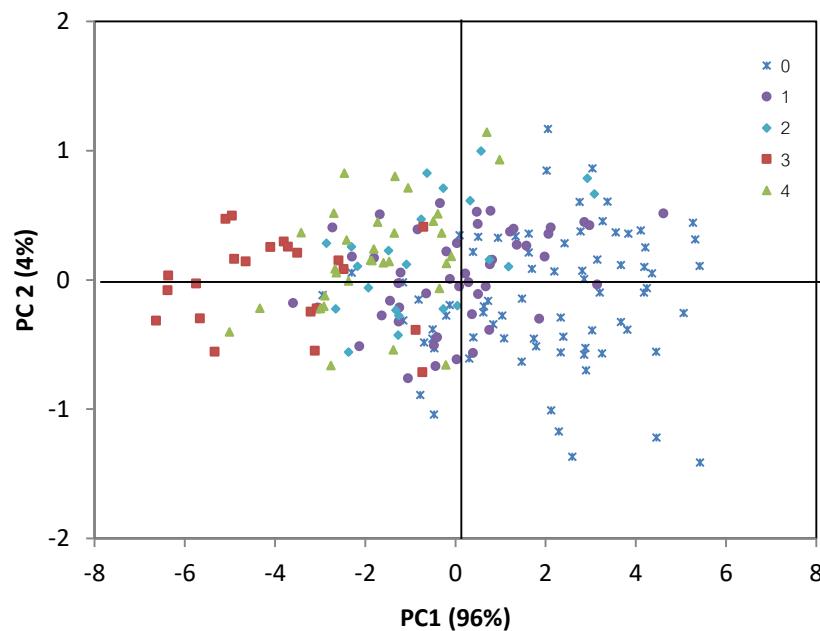


Figure 4 Result of PCA of Mandarin fruit in each group

Table 2. Dry juice sac prediction of Mandarin using MLR-DA by important wavelength and variable

wavelength and variable	normal fruits were precise predicted (75)	Dry juice sac fruits were precise predicted (125)	Accuracy in predicting (%)
962 and 978 nm	60	105	82.5
826, 924, 962, 978, 1008 and 1028 nm	71	115	93.0
826, 924, 962, 978, 1008 and 1028 nm and MC	70	117	93.5
826, 924, 962, 978, 1008 and 1028 nm and TSS	72	117	94.5
826, 924, 962, 978, 1008 and 1028 nm and TA	71	117	94.0
826, 924, 962, 978, 1008 and 1028 nm , MC, TSS and TA	72	120	96.0

4. Conclusions

Analyses using multiple linear regression - discriminant analysis (MLR-DA) Savitzky-Golay smoothing (10 nm average for left and right sides) were used as spectra pre-treatment method for the optimal MLR-DA model performance of MC, TSS and TA. The effective wavelengths in MLR-DA were at 826, 924, 962, 978, 1008, 1028 nm. The classification accuracy of MLR-DA was 96%. MLR-DA can detect dry juice sac fruits from normal fruits. It should be prepared as the Mandarin fruit used in the test covered the whole season. The same sample source with several samples can be reducing the errors of the prediction and to get a good representative testing.

Acknowledgements

The authors gratefully acknowledge the contribution of Postharvest Technology Research Center, Faculty of Agriculture, Chiang Mai University, Thailand and Postharvest Technology Innovation Center, Commission on Higher education, Thailand.

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