Malays. Appl. Biol. (2018) 47(3): 115–120

THE PREDICTION OF SHELF LIFE OF LOCAL ORANGES USING SPECTRAL INFORMATION IN UV-VISIBLE-NIR REGION COMBINED WITH PARTIAL LEAST SQUARES REGRESSION

DIDING SUHANDY[1*], DWI DIAN NOVITA[1], MEINILWITA YULIA[2], ARION OKTORA[1] and YUNI KURNIA FITRI[1]

[1]*Department of Agricultural Engineering, The University of Lampung, Jl. Soemantri Brojonegoro No. 1 Gedong Meneng Bandar Lampung, Lampung 35145, Indonesia*
[2]*Department of Agricultural Technology, Lampung State Polytechnic, Jl. Soekarno Hatta No. 10, Rajabasa Bandar Lampung, Lampung, Indonesia*
[*]*E-mail: diding.sughandy@fp.unila.ac.id*

Accepted 5 May 2018, Published online 30 June 2018

ABSTRACT

Oranges is easy to be broken during handling and long transportation. One of the most challenging issues in this supply-demand chain of oranges is to separate the fresh orange fruits from the older ones. During storage, the quantity of flavonoid substances in oranges is decreasing. In this research we investigate the potential application of using absorbance spectral information in UV-Vis-NIR region for prediction of shelf life in local orange fruits (Siam oranges from Jember) during storage. For this, we perform spectral acquisition of extracted orange samples in 1, 4, 7, 10 and 13 days of storages using a UV-Vis spectrometer in absorbance mode (Genesys^{TM} 10S UV-Vis, Thermo Scientific, USA). For extraction samples we use a 2 cm x 2 cm of peel part of oranges. The sample preparation was done with chloroform as solvent for fluorescence substance extraction purpose. The calibration model for shelf life prediction of local oranges was developed using PLS regression with full cross validation. The calibration resulted in good correlation with r = 0.89 for calibration step and r = 0.63 for validation step, respectively. The prediction using different samples resulted in root mean square error of prediction (RMSEP) = 3.34 days. It can be concluded that there is a potential application of using spectral information in UV-Vis–NIR region combined with PLS regression for shelf life prediction of local oranges.

Key words: Local oranges, chemometrics, PLS regression, calibration, UV-Vis-NIR region

INTRODUCTION

There is an increasing in the consumption of fresh food in Indonesia. Especially for citrus, the consumption has been increasing at a faster rate compared to other horticultural products. City consumers are becoming more health conscious and this has opened up opportunities for the modern retail sector to expand further into fresh foods.

Compared to 2012, citrus production in Indonesia has increased by about 40.4% to reach 2.014 million tons in 2016. Citrus represented about 10.98% of total fruit production in 2016 (Susanti & Waryanto, 2017). Five provinces dominate citrus production – North Sumatra, East Java, South Sumatra, South Sulawesi and West Kalimantan – accounting for 70% of Indonesia's production. Jember in East Java is one of the main producers of Siam citrus. Citrus from this place are traded not only in Java Island but also transported into several places in Sumatera including Lampung province. The long transportation of citrus from Jember to several places in Sumatera including Lampung provides a major challenge to distribute fresh products nationally. Most of Indonesia's locally produced fresh fruit is distributed throughout Indonesia in non-refrigerated trucks. One of the most challenging issues in this supply-demand chain of oranges is to separate the fresh orange fruits from the older ones. Some retailers may do mixing between fresh and old orange fruits in order to gain more financial benefit. So, in order to establish a fair trading and to protect our customer from any unfair trading including mixing between fresh and old

* To whom correspondence should be addressed.

products, it is very important to develop a method to detect and quantify the freshness condition in orange fruits.

It has been reported that most oranges species accumulate substantial quantities of flavonoid substances, that fluorescence under ultraviolet (UV) light (Kondo *et al.,* 2009; Benavente-Garcia *et al.,* 1993; Castillo *et al.,* 1992). The peel of the oranges fruits will fluorescence when the peel oil is released by some defects and can become visible when exposed to UV (Kondo *et al.,* 2009; Kurita *et al.,* 2009). In a recent study, Blasco *et al.* (2007) examined the use of UV-induced fluorescence as a part of a multispectral analysis to identify defects in citrus caused by the green mould. In another study Slaughter *et al*. (2008) evaluated the feasibility of using machine vision and long wave UV fluorescence to detect and separate freeze-damaged oranges.

It is also interesting that the quantities of flavonoid substances in most orange fruits are changed during storage. This information can be used to assess the freshness in orange fruits if we can obtain the information of flavonoids contents during storage. In the previous report, Suhandy *et al.* (2016) reported that there is a correlation between storage times of orange fruits with its spectral absorbance in UV-Vis region. To establish a simple method for shelf life prediction of local oranges, in this paper we use UV-Vis spectral data coupled with partial least squares (PLS) regression method to evaluate the storage time of oranges. This method may contribute to separate local oranges precisely based on appropriate storage time and predict its shelf life to establish a fair trading of local oranges.

MATERIALS AND METHODS

Sample preparation

A number of 75 orange fruits (Siam Jawa from Jember, East Java) were collected directly from fruits retailers at Bandar Lampung, Lampung, Indonesia. All samples were divided into five groups of storage (1 day, 4 day, 7 day, 10 day, and 13 day, respectively). The storage conditions were the same for every sample. These experiments were performed at room temperature (around 27–29°C).

An aqueous extraction procedure of the orange fruits was performed both for peel part and flesh part without seed. First, for peel part, a 2 cm x 2 cm area of peel was used as sample. Each sample was crushed using a mortar and mixed with 2 mL of chloroform. For flesh part without seed, weighed 1 g of the flesh and then crushed with 2 mL of chloroform. Then the samples were filtered using a 25 mm pore-sized quantitative filter paper. After cooling process to room temperature (for 20 min), all extracts were then diluted with 5 mL of chloroform. UV-Vis-NIR spectra from the aqueous extracts were acquired using a UV-Vis spectrometer (Genesys^{TM} 10S UV-Vis, Thermo Scientific, USA).

Instrumentation and measurement of spectra

The UV-Vis-NIR spectra in the range of 190-1100 nm were acquired by using a UV-Vis spectrometer (Genesys^{TM} 10S UV-Vis, Thermo Scientific, USA) equipped with a quartz cell with optical path of 10 mm, and spectral resolution of 1 nm at a room temperature. Before the measurements step, blank (the same chloroform used in extraction process) was placed inside of the blank cell to adjust the 100% transmittance line. It is noted that during spectral data measurement, all cell were closed to avoid rapid evaporation of the samples.

Data analysis

All recorded spectra data were transferred to computer via USB flash disk and then convert the spectra data from .csv extension into an excel data (.xls). The samples were divided into two groups. One group consist of 50 samples were used for developing calibration and validation model using full-cross validation method. The other group consists of 25 samples were used for performing prediction step. The calibration model and validation test for storage time prediction was developed using Partial Least Squares Regression 1 (PLSR1) for smoothing spectra. Performance of the calibration model was evaluated using following statistical parameters such as coefficient of correlation between predicted and measured storage time (r), standard error of prediction (SEP), and bias between actual and predicted storage time. The calculation of smoothing spectra, PLSR1 and prediction were done by using multivariate software of The Unscrambler® V.9.1 (CAMO AS, Trondheim, Norway).

RESULTS AND DISCUSSION

Spectra of oranges extraction samples in UV-Vis-NIR region

Figure 1 demonstrated the smoothing average spectra of extracted local oranges in the range of 190-1100 nm. We can observe very high absorbance in the range of 200–400 nm (ultraviolet range). In the visible and near infrared range we can see a small amount of absorbance. High absorbance in UV range may come from the high absorbance of flavonoid substance contained in peel part of oranges.

In order to check the quality of the obtained spectra, we perform principal components analysis (PCA) and checking the Hotelling's T2 test and

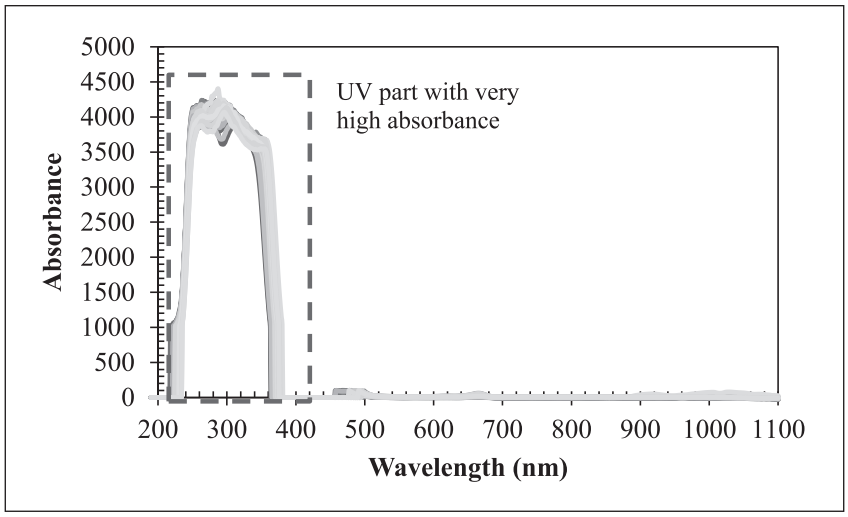

Fig. 1. Absorbance spectra of extracted local oranges fruits in the range of 190-1100 nm acquired using UV-Vis spectrometer.

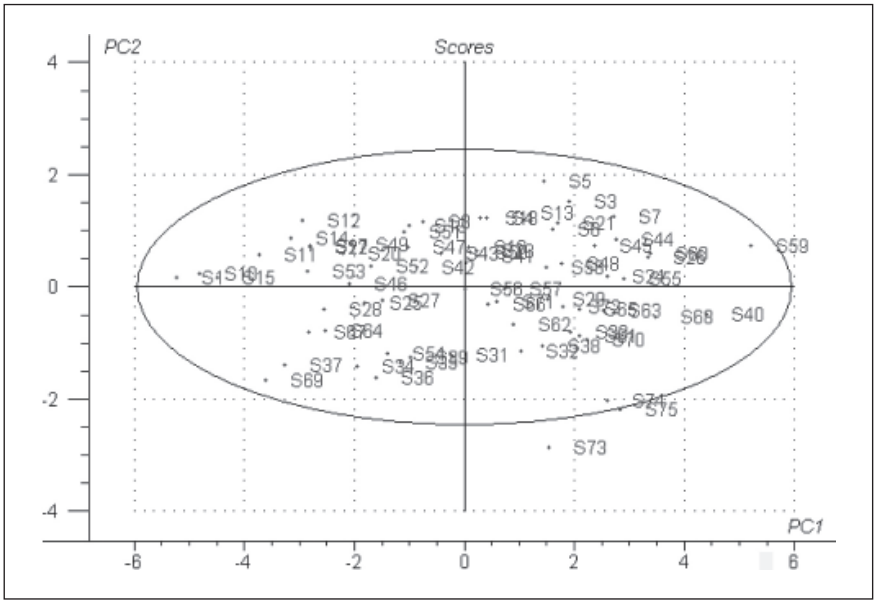

Fig. 2. Scores scatter plot with Hotelling's T2 Ellipse for local oranges in the range 190-1100 nm.

taking 95% confidence intervals (Constantinou *et al.,* 2004). Figure 2 showed the result of Hotelling's T2 test of 75 spectral data. In general we can conclude that the quality of the spectral data was quite good. It can be seen that all spectral data lied inside the ellipse. However, there four samples including sample S73 locate outside the ellipse and for this reason we omitted those sample from further modelling steps. Here, we observe that after doing Hotelling's T2 test, the calibration samples was 48 samples and the prediction samples was 23 samples, respectively.

Developing a calibration model

Using smoothing spectra (moving average smoothing with 11 segments for averaging), the calibration and validation results were very promising. Figure 3 shows the calibration results for storage time determination for local oranges. The calibration has coefficient correlation (r) = 0.89. The calibration model also had low standard error of calibration (SEC). The SEC was 1.93 day and the RMSEC was 1.91 day with low bias. From Figure 4 it is also clear that the calibration model resulted in low SEP = 3.42 day. The RMSEP was 3.39 day with

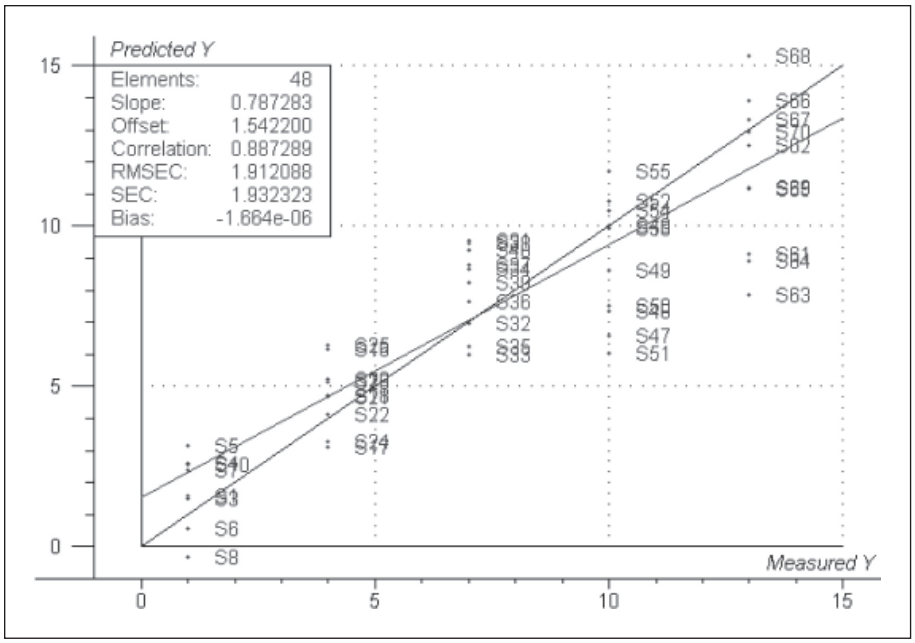

Fig. 3. The calibration result for storage time determination using smoothing average spectra in the range of 190-1100 nm.

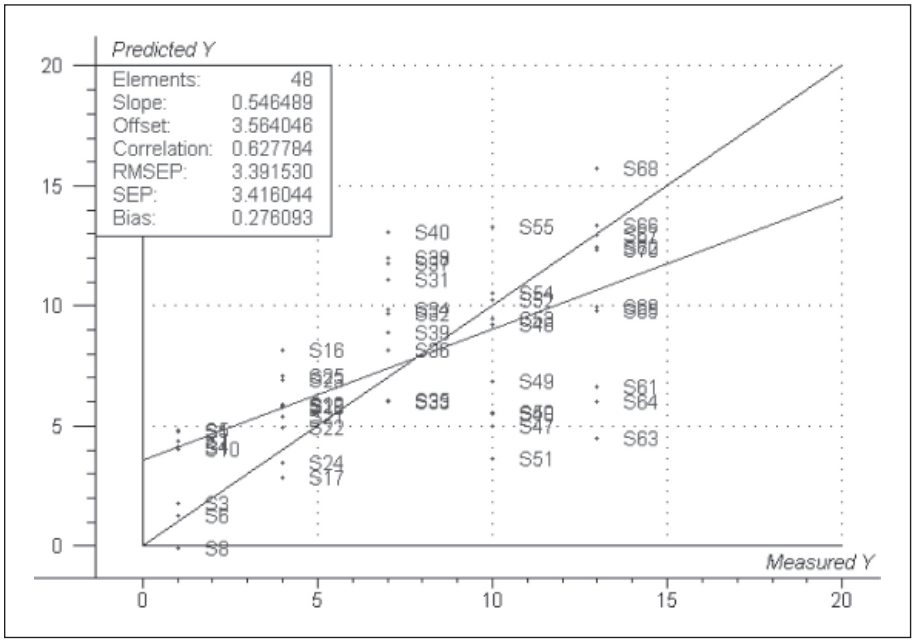

Fig. 4. The validation result for storage time determination using smoothing average spectra in the range of 190-1100 nm.

bias = 0.28 day. The quality of the calibration resulted from this study was comparable to several previous studies related to freshness estimation of agricultural products. Esquerre *et al.* (2009) used Vis/NIR spectroscopy and their developed calibration model had the root mean square error of cross validation (RMSECV) for age of mushroom 1.0 ~ 1.4 days. ElMasry *et al.* (2015) used the indicator of K-values to assess the freshness of intact frozen fish. The results revealed that freshness of frozen fish could be accurately predicted with R^2 of 0.89 and RMSECV of 9.66%. In a recent study, a low cost spectrometer was used to determine egg storage time. A regression model was established with R-squared 0.83 with RMSECV 1.97 days (Coronel-Reyes *et al.,* 2018).

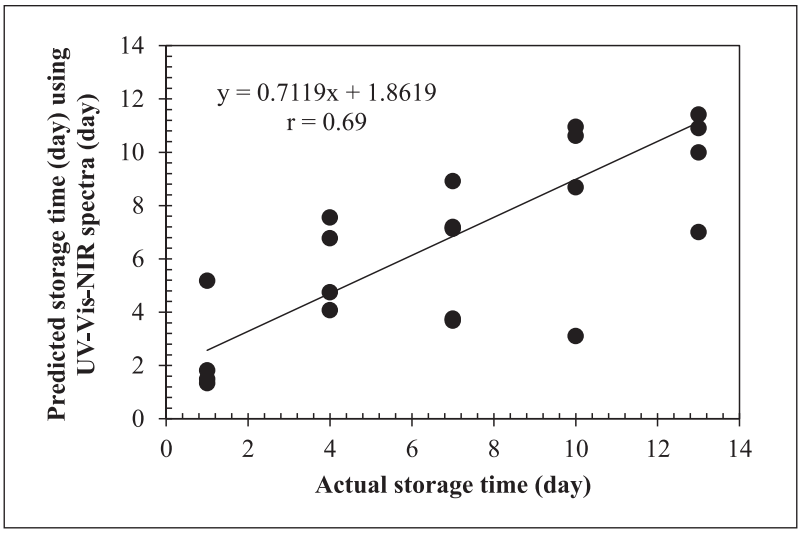

Fig. 5. The scatter plot between actual and predicted storage time in the prediction step in the range of 190-1100 nm.

Prediction of storage time using developed calibration model

Figure 5 showed the result of prediction step. It showed the scatter plot between actual storage time and predicted storage time (day). We can see that there is a promising result with coefficient of correlation between actual and predicted storage time was 0.69. Increasing number of samples in the prediction step may improve the quality of prediction with higher coefficient of correlation. The RMSEP in prediction step was 3.34 day and bias was -0.12 day.

CONCLUSION

The calibration and validation was developed in the range of 190–1100 nm and resulted in high coefficient of correlation (r) = 0.89. The storage time of local oranges were then predicted using the developed calibration model and resulted in promising coefficient of correlation (r) = 0.69. In this research we successfully show that there is a potential application of using spectral absorbance in UV-Vis-NIR region of extracted local oranges to predict storage time (day) of local oranges. This method may be useful to establish a technology to predict shelf life of local oranges and define freshness of local oranges based on the decreasing of flavonoid substances.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge support of the Indonesian Ministry of Research, Technology and Higher Education (KEMENRISTEKDIKTI) via Hibah Fundamental 2016 (Nomor: 76/UN26/8/LPPM/2016) and The University of Lampung, Indonesia. We also thank to the Department of Agricultural Engineering, The University of Lampung for their permission to use their facilities for spectral data acquisition.

REFERENCES

Benavente-Garcia, O., Castillo, J. & Del Rio, J.A. 1993. Changes in neodiosmin levels during the development of Citrus aurantium leaves and fruits postulation of a neodiosmin biosynthetic pathway. *Journal of Agricultural and Food Chemistry*, **41**(**11**): 1916-1919.

Blasco, J., Aleixos, N., Gomez, J. & Molto, E. 2007. Citrus sorting by identification of the most common defects using multispectral computer vision. *Journal of Food Engineering*, **83**(**3**): 384-393.

Castillo, J., Benavente, O. & Del Rio, J.A. 1992. Naringin and neohesperidin levels during development of leaves, flower buds, and fruits of Citrus aurantium. *Plant Physiology*, **99**(**1**): 67-73.

Constantinou, M.A., Papakonstantinou, E., Benaki, D., Spraul, M., Shulpis, K. & Koupparis, M.A. 2004. Application of nuclear magnetic resonance spectroscopy combined with principal component analysis in detecting inborn errors of metabolism using blood spots: a metabonomic approach. *Analytica Chimica Acta*, **511**(**2**): 303-312.

Coronel-Reyes, J., Ramirez-Morales, I., Fernandez-Blanco, E., Rivero, D. & Pazos, A. 2018. Determination of egg storage time at room

temperature using a low-cost NIR spectrometer and machine learning techniques. *Computers and Electronics in Agriculture*, **145**: 1-10.

ElMasry, G., Nagai, H., Moria, K., Nakazawa, N., Tsuta, M., Sugiyama, J., Okazaki, E. & Nakauchi, S. 2015. Freshness estimation of intact frozen fish using fluorescence spectroscopy and chemometrics of excitation-emission matrix. *Talanta*, **143**: 145-156.

Esquerre, C., Gowen, A.A., O'Donnell, C.P. & Downey, G. 2009. Initial studies on the quantitation of bruise damage and freshness in mushrooms using visible-near-infrared spectroscopy. *Journal of Agricultural and Food Chemistry*, **57(5)**: 1903-1907.

Kondo, N., Kuramoto, M., Shimizu, H., Ogawa, Y., Kurita, M., Nishizu, T., Chong, K.V. & Yamamoto, K. 2009. Identification of fluorescent substance in mandarin orange skin for machine vision system to detect rotten citrus fruits. *Engineering in Agriculture, Environment and Food*, **2**(**2**): 54-59.

Kurita, M., Kondo, N., Shimizu, H., Ling, P., Falzea, P.D., Shiigi, T., Ninomiya, K., Nishizu, K. & Yamamoto, K. 2009. A double image acquisition system with visible and UV LEDs for citrus fruit. *Journal of Robotics and Mechatronics*, **21**(**4**): 533-540.

Slaughter, D.C., Obenland, D.M., Thompson, J., Arpaia, M.L. & Margosan, D.A. 2008. Non-destructive freeze damage detection in oranges using machine vision and ultraviolet fluorescence. *Postharvest Biological Technology*, **48**(**3**): 341-346.

Suhandy, D., Novita, D.D., Yulia, M., Oktora, A. & Fitri, Y.K. 2016. The potential application of using information from absorbance spectra in UV-Vis region for prediction of shelf life in local orange fruits during storage. Proceedings of National Seminar on Tempe, Bandar Lampung, Indonesia.

Susanti, A.A. & Waryanto, B. 2017. Agricultural Statistics 2017. http://epublikasi.setjen.pertanian.go.id/download/file/367-statistik-pertanian-2017.