Infrared Spectroscopy for Non-destructive and Fast Identification of Artificially Ripened Papaya (*Carica papaya*)

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Abstract

Papaya, the second most consumed fruit in Sri Lanka, is well adapted to all agro climatic zones with high annual production. However, the export amount is less than 2% of the total production due to poor post-harvest processing measures including artificial ripening. Therefore, an attempt was made to use the Near Infrared Spectroscopy (NIRS) for the detection of artificially ripened papaya by Calcium Carbide and Ethephon. Calcium Carbide and Ethephon were applied for artificially ripening of papaya fruits including controls with natural ripening. Each treatment was replicated four times consisting four fruits per each replicate. The fruits were arranged in plastic crates padding with polyurethane foam layer in 36 mm of thickness. Five near infrared spectra per fruit per day were acquired from all papaya samples until the fruits were overripe. Spectral data were pretreated to reduce impacts of environmental noise. Soft Independent Modelling of Class Analogy (SIMCA) calibration models (Pirouette Infometrix, Woodinville, WA, USA) were developed to identify the artificially ripened fruits from the controls. The predictions were accurate as 100%, 95.2% and 98.4% in control samples, CaC_2 and Ethephon treated samples, respectively. Partial Least Square models were also developed to predict the Brix and Firmness values of fruits at ripening. Brix and firmness values were accounted 8.3 and 0.86 correlation coefficients for PLS regression Y fit, respectively. The research revealed that the potential possibility of using NIR technology as a nondestructive identification tool for artificially ripened papaya fruits using CaC_2 and Ethephon.

Keywords: Artificial ripening, Ethephon, NIR Spectroscopy, Papaya

Introduction

Sri Lanka has promising potential as an exporter of a wide range of high-value fruits year round because of its diverse tropical climate with two monsoons and fertile soils. Papaya is well adapted to all agro climatic zones with high annual production (Farzana, 2008). However, the export volume of papaya is very low as 2% from total production though the production is high as 19754 Mt/annum (Mannapperuma, 2004). There is a big demand for Sri Lankan papaya, especially variety Rathna, in the world market as the European Union has increased papaya imports by 135% within three years since 2002 (DOA, 2006). Though the countries are increasingly excited at Sri Lanka's potential to capture a larger share of fruit market but also frustrated by their inability to access greater quantities of export-quality fruits.

Use of Calcium Carbide and Ethephon in artificial ripening of papaya is one of the main barriers for Sri Lanka to promote the export of fresh papaya fruit industry. The application of such chemicals not only degrades the natural taste and nutritional value of fruits but also brings serious economic impacts to the country due to its direct implications on human health and international trade. Especially Calcium Carbide contains traces of Arsenic and Phosphorus that can cause high health risk to human body (Chace, 1994).

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The development of our fresh fruit market, both local and export-oriented, is mainly hindered by inadequate technologies for processing and value addition. Postharvest sorting and grading is difficult and labor intensive. Therefore, non-destructive measuring techniques are desirable for fruit and vegetable industry as they are fast, chemical free and multiple detection possibilities with minimum operational cost. Near Infrared Spectroscopy (NIRS) is a non-destructive technique appropriate for fruit quality detection, but there is no report on application of NIR in non-destructive identification of artificially ripened papaya in Sri Lanka. Therefore, the objective of this study was to use NIRS for the identification of artificially ripened Papaya with CaC_2 and Ethephon from the control samples of naturally ripened.

Materials and methods

Forty eight fruits of moderately grown papaya variety Rathna were carefully selected by considering their weight and shape for uniformity and placed randomly in plastic containers 530 × 350 × 300 mm in size. Four fruits were kept in a single plastic container after padded them with 36mm thick polyurethane foam to prevent possible mechanical injury. Each treatment consisting four replicates with four fruits per each replicate. Sixteen papaya fruits kept in four containers were treated with Calcium Carbide (CaC_2) at a rate of 1.2g/100g fruit weight. Small plastic 100 x 100 x 30 mm cup filled with 100ml of distilled water layer was kept inside the containers to increase the humidity near CaC_2 was stored. Fruits were wrapped with a paper to avoid direct contaminations after they were stored. Another sixteen papaya fruits, kept in four containers were treated with Ethephon at a rate of 0.5 g/L distilled water. The rest of the sixteen fruits in the other four containers were kept as controller. Ethephon solutions were sprayed on fruit surfaces.

NIR Spectrometer FQA-NIR Gun (Shibuya Seiki, Hamamatsu, Japan) was used to acquire five NIR reflectance spectra per fruit per day and continued until the fruits become overripe. The acquired spectra were first evaluated by principal component analysis for removing the possible outliers. Spectra from untreated, treated with CaC_2 and Ethephon were assigned as discriminate class 1, 2 and 3, respectively in the Soft Independent Modelling of Class Analogy (SIMCA) to make calibration models for the sample identification.

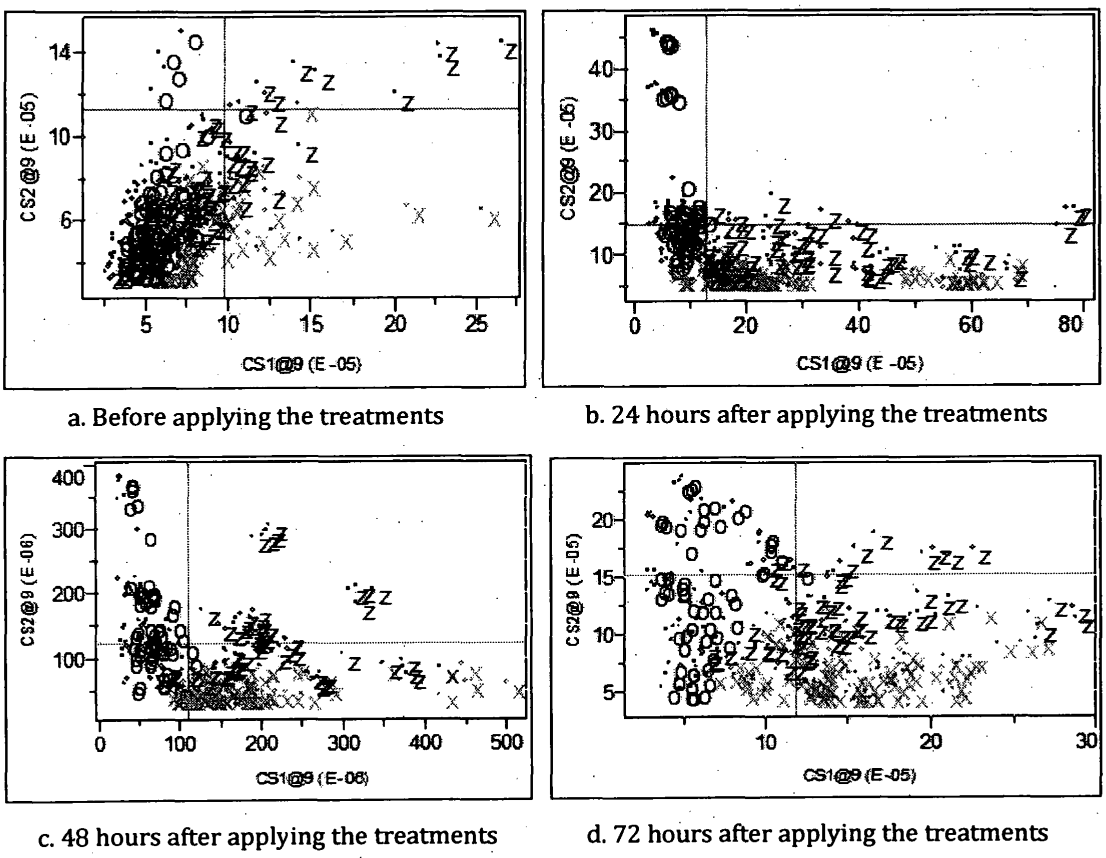
After the spectral data acquisition, the samples were used to investigate for their Brix and Firmness values. The Brix values were obtained from the papaya juice extracted on to the optical refractometer. The fruit firmness values were taken by using mechanical penetromater. As this procedure was destructive, the Brix and Firmness values of fruits were taken only once at the end of the experiment. Partial Least Square models were developed to predict the Brix and Firmness values at their final stage of ripening.

Results and discussion

During the model development process, it was found that applying first derivative and smoothing data pre-treatments to the raw spectra described the samples better than the raw spectra. As such the analyses were done under the above two spectral data transformations.

Changes of quality attributes of papaya fruits under three different ripening environments are illustrated in Figure 1, in two dimensional principal component space. As shown in the Fig.1, (a), the statistical distance i.e class distance of two treatments to the control were very small. The class distance of control samples (O) to the treatment Ethephon applied samples (Z) was 0.83 and to the treatment of Calcium Carbide applied samples (X) was 0.45. The samples belonging to three groups were observed locating altogether in the same principal component space without clear separation. This indicates that the fruits were having almost similar properties before applying the treatments. After 12 hours, in Fig.1.(b), the respective statistical distance figures to the control were increased to 3.86 and 2.85 as Ethephon and Calcium Carbide applied samples, respectively. This indicates that the higher response of papaya fruits to the Ethephon for their postharvest quality changes when it is compared with the Calcium Carbide applied samples. This trend was further continued as the distances were increased similarly up to 4.9 and 2.8 to the control during next 24 hours. After 72 hours, the class distance for both treatments to the controls were declined to 2.53 to 1.23 Ethephon and Calcium Carbide applied samples, respectively due to all papaya samples become overripe. However the above mentioned trend has maintained.

Table 1. explains the prediction performance of fruit samples belonging to each category. As it was shown, 35 samples (14+11+10) belonging to three categories were misclassified before applying the treatments. However this was fairly good (over 80 % of correct) classification before applying the treatments and seems undesirable as it indicates considerable variation between three categories of papaya even before applying the treatments. However, this argument has been answered by the small statistical distance reported (0.83) Ethephon treated and (0.45) Calcium Carbide treated before applying the treatments. As a rule of thumb, the class distance should be greater than 3 to consider a sample group as a separate population.



a. Before applying the treatments

b. 24 hours after applying the treatments

c. 48 hours after applying the treatments

d. 72 hours after applying the treatments

Figure 1. Distribution of sample in two dimensional principal component space over the time. Control (O) Ethephon treated (Z) Calcium Carbide treated (X)

The class distances as well as the classification rates were rapidly improved 24 hours after applying the treatments as the rates were accurate as 100%, 95.2% and 98.4% in control treatments, CaC_2 and Ethephon respectively. Constructed PLS regression for Brix and Firmness values were with fairly good correlation coefficients i.e. of 0.83 and 0.86, respectively.

Conclusions

The developed spectra calibration model of Soft Independent Modeling of Class Analogy (SIMCA), classified the artificially ripened papaya successfully at the rates of 100%, 95.24% & 98.4% as controller, CaC_2 and Ethephon, respectively. The results indicated that the higher response of papaya fruits to the Ethephon for their post harvest quality changes when it is compared with the Calcium Carbide applied samples at the investigated application rates. PLS models constructed for Brix and Firmness values were with fairly good correlation coefficients of 0.85 and 0.86 respectively with their regression.

The research revealed that the potential possibility using NIR technology as a nondestructive identification tool for artificially ripened papaya fruits by using CaC_2 and Ethephon.

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Table 1. SIMCA Prediction performances of fruits at artificial ripening

Time	Treatment	Total samples	Correct classification	Error dassification	Prediction rate
	Control	70	56	14	80.00
	CaC_2	70	59	11	84.29
Before Treatment	Ethephon	69	59	10	85.51
	Control	65	65	0	100.00
24 hours after treatment	CaC_2	63	60	3	95.24
	Ethephon	62	61	1	98.39
	Control	64	62	2	96.88
48 hours after treatment	CaC_2	63	62	1	98.41
	Ethephon	61	59	2	96.72
	Control	59	59	0	100.00
72 hours after treatment	CaC_2	61	53	8	86.89
	Ethephon	63	62	1	98.41