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Research Paper

Vis/NIR spectroscopy and chemometrics for the prediction of soluble solids content and acidity (pH) of kiwifruit

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Visible and near infrared spectroscopic (Vis/NIRS) techniques have shown promise as rapid and non-destructive tools to evaluate the various internal quality attributes of fruits and vegetables. The objective of this study was to develop a calibration model for prediction of soluble solids content and acidity (pH) of kiwifruit by using visible and near infrared spectroscopy and chemometrics. The transmission spectra of kiwifruit were obtained in the wavelength range from 400 to 1000 nm. The effects of different pre-processing methods and spectra treatments, such as standard normal variate transformation (SNV), multiplicative scatter correction (MSC), and median filter and first derivative (D^1) were analysed. The prediction models were developed by principal component analysis (PCA) and partial least square regression (PLS). The correlation coefficient for soluble solids content and pH were 0.93, 0.943 and root mean square error of prediction (RMSEP) was 0.259Brix and 0.076, respectively. These results were achieved when SNV was utilised in conjunction with median filter and first derivative. This showed the capability of Vis/NIRS and the important role of chemometrics in developing accurate models for the prediction of kiwifruit internal quality characteristics.

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1. Introduction

In the food industry, the quality evaluation of fruits and vegetables is an important issue. The assessment of ripeness is a major part of quality evaluation and depends on several factors such as soluble solid content (SSC), acidity (pH), etc. Most of the methods to measure these qualities are based on the complex processing of samples, using expensive chemical reagents and involving a considerable amount of manual work. Furthermore, they are still destructive. Therefore, it is essential to develop efficient and non-destructive methods for measuring the internal attributes of fruit. Near infrared

spectroscopy (NIRS) is a fast, easy-to-use and non-destructive analytical technique (Day & Fearn, 1982). One of the main advantages of NIRS is that allows several constituents to be evaluated at the same time. In addition, calibrated instruments can be used for days or months inside or outside laboratory environment. NIRS has been used to assess the internal quality of fruits and vegetables such as apple, (Fan, Zha, Du, & Gao, 2009; He, Li, & Shao, 2006; Lu, Guyer, & Beaudry, 2000; McGlone, Jordan, & Martinsen, 2002; Yan-de, Yi-bin, Xiaping, & Huishan, 2007) pear, (Fu, Ying, Lu, & Xu, 2007; Nicolaï et al., 2008; Sirisomboon, Tanaka, Fujita, & Kojima, 2007) kiwifruit, (Clark et al., 2004; McGlone, Jordan,

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Nomenclature

NIR	near infrared
VIS	visible
NIRS	near infrared spectroscopy
SSC	soluble solids content
SNV	standard normal variate
MSC	multiplicative scatter correction

D^1, D^2	first and second derivative
PCA	principal component analysis
PCR	principal component regression
PLS	partial least square
RMSEP	root mean square error of prediction
RMSECV	root mean squared error of cross validation
R_p^2	correlations of prediction sets
SEP	standard error of prediction

Seelye, & Martinsen, 2002b; Schaare & Fraser, 2000) peach, (Carlomagno, Capozzo, Attolico, & Distante, 2004; Golic & Walsh, 2006; Peiris, Dull, Leffler, & Kays, 1998; Slaughter, 1995) tomato, (Jha & Matsuoka, 2004; Pedro & Ferreira, 2005; Shao et al., 2007) and avocado (Clark, McGlone, Requejo, White, & Woolf, 2003b).

NIRS instrumentation has developed in response to the need for speed in analyses and flexibility in adapting to different sample states. However, modern NIRS provides a large amount of spectral data that contains noise and is influenced by a number of physical, chemical, and structural variables. In addition, it is difficult to distinguish subtle spectral differences between samples (Blanco & Villarroya, 2002). Because of these reasons, NIRS requires chemometrics, which is the art of drawing conclusions and extracting information from noisy data (Wold, 1995). As Blanco and Villarroya (2002) stated, NIRS would never have been at its present stage of development without chemometrics.

Researchers have studied different integral parts of chemometrics such as different pre-processing techniques, variable-reduction methods, multivariate calibration methods, and different NIRS modes (including reflectance, interactance and transmission mode), in order to construct accurate and reliable models.

Schaare and Fraser (2000) compared three modes of visible–near infrared spectroscopic measurement (Vis/NIRS) (reflectance, interactance and transmission) for their ability to non-destructively estimate harvest soluble solids content (SSC), density and internal flesh colour of the yellow-fleshed kiwifruit (*Actinidia chinensis*). They found that the spectra of interactance mode provided the most accurate estimates of SSC, density and flesh colour. Although the interactance mode provides more accurate estimation of kiwifruit attributes than reflectance and transmittance modes, obtaining a light seal may be difficult at the high conveyor speeds used in current fruit grading systems. Reflectance and transmittance modes are therefore more common than the interactance mode in online sorting systems. Kavdir, Buyukcan, Lu, Kocabiyik, and Seker (2009) obtained better results for prediction of olive firmness in transmittance mode rather than reflectance mode. The coefficient of determination (R^2) and the root mean squared error of cross validation (RMSECV) were 0.77 and 1.36, respectively. It was concluded that choosing proper fruit orientation and lamp source arrangement in transmission mode could lead to more precision models. Clark, McGlone, and Jordan (2003) investigated four arrangements of light source, apple-orientation and detector for transmission mode. Their calibration models gave correlations of prediction sets (R_p^2) of between 0.69 and 0.91 for the different geometries

across the full range of affected fruit. The best individual model was achieved when the stem–calyx axis was horizontal and the light source and detector were located at right angles to one another at the equator. They pointed out that more techniques were required for NIRS transmittance measurements in order to reduce the prediction error and produce an optimal grading system.

Fan et al. (2009) used multi lamps and second derivative as a pre-processing technique in order to improve the precision determination of firmness and SSC of Red Fuji apples by Vis/NIRS transmittance. Their validation models for SSC and firmness had a r^2 of 0.9532 and 0.8136, as well as, standard error of prediction (SEP) of 0.3838 and 0.5344, respectively.

Muik et al. (2004) optimised partial least square (PLS) models using cross validation and different pre-treatments, including mean centring, variance scaling, multiplicative signal correction (MSC), Savitzky–Golay smoothing, and first and second derivatives. They compared the effect of each pre-processing based on the root mean square error of prediction (RMSEP). The first derivative was the best pre-processing method for both oil and water content and this led to significant minimisation of the number of factors and therefore simplified the models.

Based on the previous studies, it would be expected that the transmission mode could provide better evaluation of fruit internal quality. However, in transmission mode the amount of light penetrating the fruit is very small which results in a reduced signal-to-noise ratio (Schaare & Fraser, 2000). In order to overcome this difficulty, and to make accurate prediction models, pre-processing of NIRS spectra is essential in multivariate calibration. Nevertheless, NIRS pre-processing techniques still involves trial and error, because researchers do not have sufficient information on the characteristics of pre-processing methods and have difficulties in choosing the most appropriate methods (Xu et al., 2008). The objective of this study was to evaluate the feasibility of using NIRS along with chemometrics to predict SSC and acidity (pH) of kiwifruit in a non-destructive manner, in addition to investigating the effects of different combination of pre-processing methods.

2. Materials and methods

2.1. Sample preparation

The 100 ‘Hayward’ kiwifruit used in this study were randomly divided into two groups of samples: the first group was used to develop the calibration models (70 samples) and the other for predicting quality and model validation purposes (30

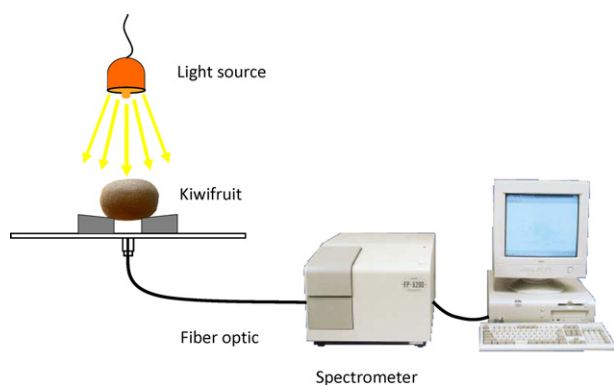


Fig. 1 – Schematic diagram of spectra detection system.

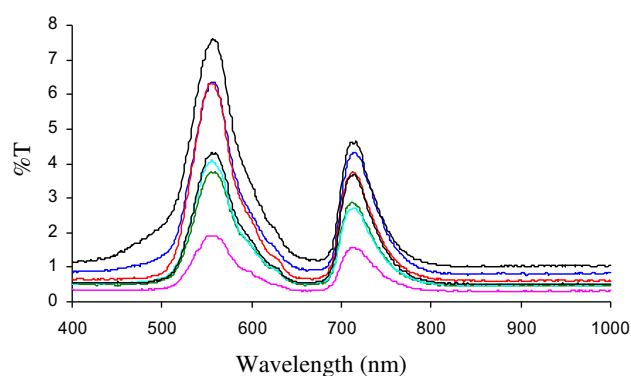


Fig. 2 – Original transmission spectra of some kiwifruit samples.

samples). All samples had been planted in the same environmental conditions and grown under similar horticultural management, and were hand harvested during one day. Then, they were individually numbered and stored for 2 days at 20 °C and 60% relative humidity.

After acquisition of spectra, SSC measurement was made with a digital refractometer (Schmidt + Haensch, Berlin, Germany) and pH of samples was measured by a pH meter (Hanna HI model 8519, Padova, Italy). All experiments, including spectra acquisition and quality analysis, were carried out on the same day.

2.2. Spectra acquisition

A tungsten halogen lamp 300 W (Osram, Munich, Germany) which emitted visible and infrared radiation was placed at a distance of 50 mm from the fruit surface. The light source was movable, so that samples with different size were placed at desired distance with the stem–calyx axis of fruits horizontal. The transmitted light was guided to a detector by a fibre optic that had a 4 mm² active surface (Fig. 1). The spectra were recorded from 400 to 1000 nm at intervals of 1 nm over 2 min including fruit handling, spectra acquisition and data storage, using a spectrometer (Jasco FP-6200, Tokyo, Japan) equipped with Spectra Manager™ software for Windows® (Jasco, Tokyo, Japan) (see Fig. 2). A fruit holder with a flexible shield between fruit sample and fibre probe, which acted as a light seal against light source, was used.

2.3. Chemometrics

Water, which is the most important chemical constituent of most fruit and vegetables, strongly absorbs near infrared radiation (Nicolai et al., 2007). The near infrared spectrum is essentially composed of a large set of overtones and combination bands. In addition, complex chemical composition of a typical fruit or vegetable causes the near infrared spectrum to be highly convoluted. The spectrum may further be complicated by wavelength dependent scattering effects, tissue heterogeneities, instrumental noise, ambient effects and other sources of variability (Nicolai et al., 2007).

Consequently, NIRS requires chemometrics to extract as much relevant information as possible from the analytical data (Blanco & Villarroya, 2002). Chemometrics has been used to extend and improve the potential application of NIRS technique in food industry (Cen & He, 2007).

Chemometrics is the science of relating measurements made on a chemical system or process to the state of the system via application of mathematical or statistical methods. Chemometrics in NIRS analysis includes three facets: (1) spectral data pre-processing; (2) building calibration models for quantitative and qualitative analysis; (3) model transfer (Cen & He, 2007). This study has focused on spectral data pre-processing and the calibration models for quantitative and qualitative analysis.

2.3.1. Pre-processing

A large amount of spectral data is usually obtained from NIR instruments and yields useful analytical information (Blanco & Villarroya, 2002; Osborne, Fearn, & Hindle, 1993). However, the data acquired from NIR spectrometer contains background information and noise besides sample information. In order to obtain reliable, accurate and stable calibration models, it is very necessary to pre-process spectral data before modelling (Cen & He, 2007). Spectral pre-processing techniques are required to remove any irrelevant information including noise, uncertainties, variability, interactions and unrecognised features. A lot of pre-processing techniques for spectral data have been developed recently. In this study several pre-processing methods were used such as normalisation (multiplicative scatter correction (MSC), standard normal variate transformation (SNV)), smoothing (median filter, Savitzky–Golay and wavelet), differentiation (first derivative and second derivative) and pre-treatment (mean centre). Normalisation is designed to remove multiplicative spectral effects. In normalisation, the spectral vector is transformed into unit length (Swierenga et al., 1999). Several smoothing techniques have been proposed to remove random noise from NIR spectra, including moving average filters and the Savitzky–Golay algorithm (Næs, Isaksson, Fearn, & Davies, 2004; Nicolai et al., 2007). It is crucial to choose the proper smoothing window width. Smoothing is also necessary in order to optimise the signal-to-noise ratio (Cen & He, 2007;

Table 1 – Statistical properties of SSC and pH.

Characteristic	Sample set	Mean	Standard deviation	Median	Maximum	Minimum	No. of samples
SSC	Calibration set	13.26	0.79	13.28	15.68	11.42	67
	Prediction set	13.19	0.64	13.18	14.5	11.92	30
pH	Calibration set	3.46	0.32	3.45	4.13	2.74	69
	Prediction set	3.47	0.21	3.47	3.94	3.02	20

Perkin, Tenge, & Honigs, 1988). Generally, it is combined with other pre-processing methods to accomplish the de-noising (Cen & He, 2007; Pontes et al., 2006; Wang, Lee, Wang, & He, 2006). Another pre-processing method including the first and second derivative is used to remove background and increase spectral resolution (Cen & He, 2007). First derivatives are applied to remove additive baseline effects and second derivatives are used to remove sloped additive baselines (Swierenga et al., 1999). All pre-processing techniques and calibration methods were carried out using ParLeS software version 3.1 (Viscarra Rossel, 2008).

In addition to pre-treatment methods like mean centre, different pre-processing techniques in the ParLeS software were divided into three categories including light scatter/baseline corrections (MSC, SNV, SNV with detrending, wavelet detrending and SNV with wavelet detrending), de-noising/smoothing (Median filter, Savitzky–Golay filter and wavelet filter) and differentiation (first and second derivative).

2.3.2. Calibration methods

Because of the vast amount of spectral information provided by NIR spectrophotometers, the large number of samples required to build classification and calibration models, and the high correlation in spectra, there is a need for variable-reduction methods that allow the dimensions of the original data to be reduced to a few uncorrelated variables containing only relevant information from the samples. The best known, and most widely used, is principal component analysis (PCA) (Blanco & Villarroya, 2002). PCA searches for directions of maximum variability in sample grouping and uses them as new axes called principle components that can be used as new variables, instead of the original data, in following calculations (Blanco & Villarroya, 2002; Cowe & McNicol, 1985). PCA was performed for a maximum of 10 principal components. PCA showed that there were some spectral outliers in each calibration data set. These samples were identified and removed before modelling by PLS regression.

The multivariate-regression methods most frequently used in NIR spectroscopy are principal component regression (PCR) and PLS regression (Martens & Næs, 1989). PLS models are slightly better than the PCR because they do not include latent variables that are less important to describe the variance of the quality parameter (Jong, 1993). As a result, the PLS method was used to develop calibration models to predict SSC and pH of kiwifruit. PLS found the directions of greatest variability by considering both spectral and measured property information, with the new axes, called PLS factors (Blanco & Villarroya, 2002). The correct number of regression factors for the PLS model was determined according to the minimum

root mean square error of cross validation (RMSECV). A low number of factors were desirable in order to avoid inclusion of signal noise in the modelling (Xiaobo, Jiewen, Xingyi, & Yanxiao, 2007).

The prediction error of the calibration model was defined for different sample set as the root mean square error of prediction (RMSEP)

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n_p} (\hat{y}_i - y_i)^2}{n_p}} \quad (1)$$

where \hat{y}_i is the predicted value of the i th observation, y_i is the measured value of the i th observation and n_p is the number of observations in prediction set.

3. Results and discussions

Table 1 shows the summary statistics for all samples selected in each data set. During the construction of the calibration models, PCA was used to detect those samples that can affect the model performance. Three samples for SSC and one sample for pH were left out, due to their potential bad influences over the models.

3.1. Effects of different pre-processing

Various calibration models were developed by using different pre-processing techniques on the spectral data. Each calibration model was used to predict SSC and pH of prediction data set in order to verify the improved ability of models based on different pre-processing techniques. A proper model should

Table 2 – The prediction results of SSC with different pre-processing techniques.

Pre-processing	No. of PLS factor	r	RMSEP
Original data	10	0.60	0.551
SNV, Median filter, D ¹	9	0.93	0.259
SNV, Savitzky–Golay, D ¹	10	0.796	0.386
SNV, Wavelet, D ¹	6	0.791	0.401
SNV, Median filter, D ²	8	0.657	0.765
SNV, Median filter, D ¹ and mean centre	8	0.92	0.262
SNV, Median filter, D ² and mean centre	5	0.905	0.271
MSC, Median filter, D ¹	9	0.921	0.474
MSC, Savitzky–Golay, D ¹	9	0.798	0.388
MSC, Wavelet, D ¹	6	0.824	0.673
MSC, Median filter, D ² and mean centre	4	0.904	0.272

Table 3 – The prediction results of pH with different pre-processing techniques.

Pre-processing	No. of PLS factor	r	RMSEP
Original data	10	0.808	0.142
SNV, Median filter, D ¹	9	0.943	0.076
SNV, Savitzky–Golay, D ¹	10	0.936	0.086
SNV, Wavelet, D ¹	10	0.926	0.097
SNV, Median filter, D ²	8	0.791	0.162
SNV, Median filter, D ¹ and mean centre	8	0.934	0.08
SNV, Median filter, D ² and mean centre	7	0.928	0.088
MSC, Median filter, D ¹	9	0.943	0.244
MSC, Savitzky–Golay, D ¹	10	0.945	0.214
MSC, Wavelet, D ¹	10	0.904	0.235
MSC, Median filter, D ² and mean centre	10	0.93	0.085

have a low RMSEP and a high correlation coefficient between the predicted and measured value of each property. Moreover, a low number of PLS factors are desirable. Models have been developed using different number of PLS factors and different

combination of pre-processing techniques. However, only the most accurate models were presented in Tables 2 and 3 with their correlation coefficient and RMSEP.

If no pre-processing was applied, a minimum correlation coefficient was observed in the 10 factor PLS model for prediction of either SSC or pH. However, if pre-processing was applied, correlation coefficient increases and the RMSEP was reduced. In the meantime it was found that the number of PLS factors could be reduced by the use of data pre-processing. SNV in combination with median filter and first derivative was the best pre-processing method. This combination increased correlation coefficient from 0.6 to 0.93 and from 0.808 to 0.943 for prediction of SSC and pH, respectively whilst the RMSEP decreased from 0.551 to 0.259 for SSC and from 0.142 to 0.076 for pH. Furthermore, the number of PLS factors dropped to 9.

It can be concluded that different pre-processing techniques had effects on the prediction performance of the model using PCA and PLS methods. The best pre-processing of normalisation, smoothing and derivative is shown Fig. 3. The average of all spectra from the kiwifruit can also be seen in Fig. 3(a) where the original data and pre-processed data are compared. SNV and MSC were better than the other light

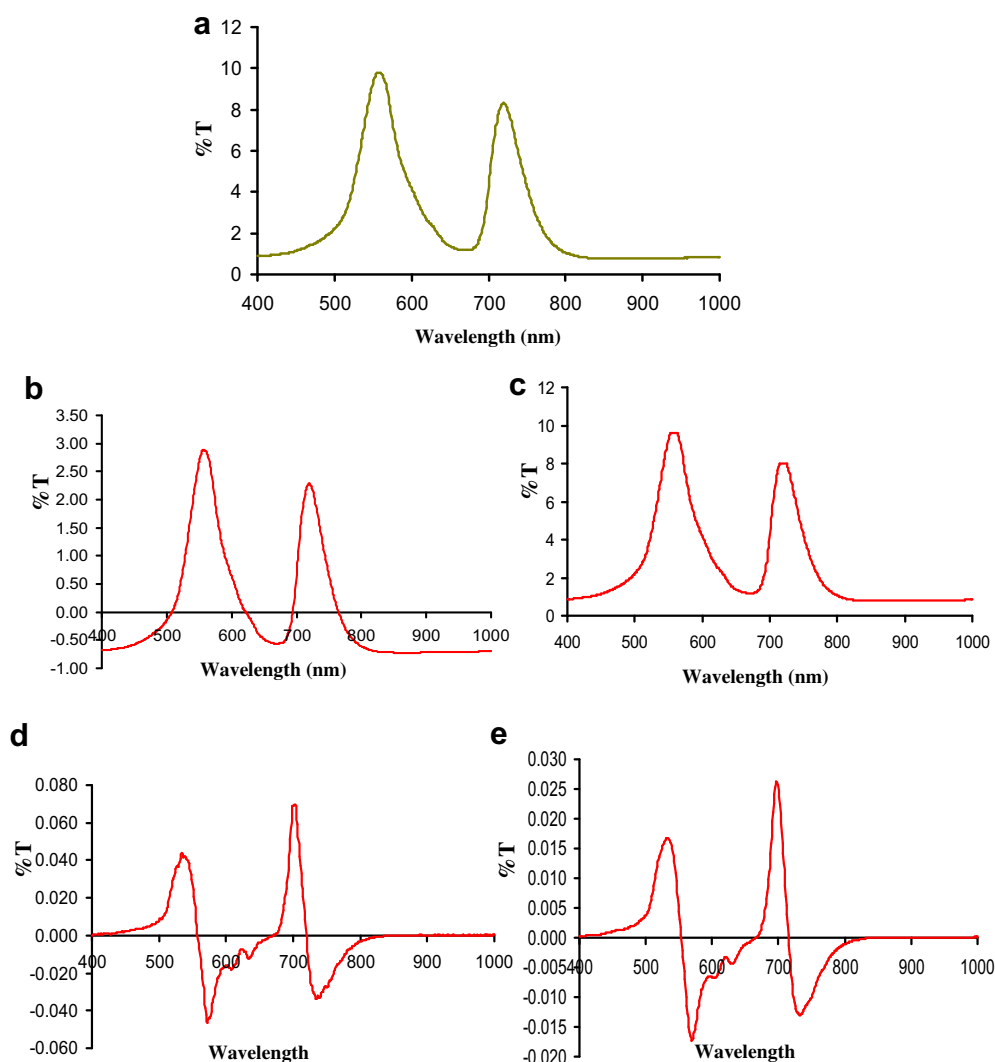


Fig. 3 – NIR spectra of kiwifruit samples obtained from: (a) average from raw spectra of all samples, (b) SNV, (c) median filter, (d) D¹, and (e) combination of SNV, median filter and D¹.

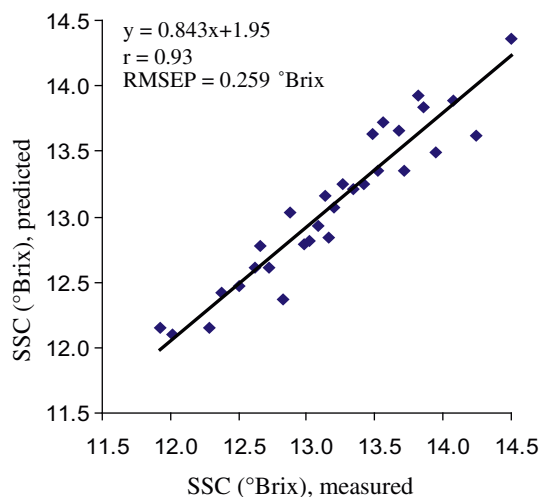
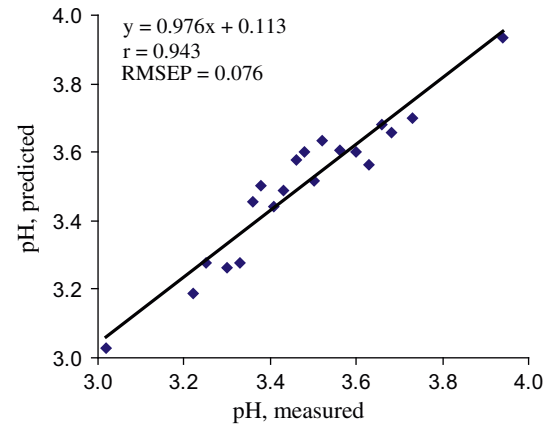
Table 4 – The prediction results for different median filter ranks in conjunction with SNV and D¹.

Characteristic	Prediction Parameter	Median filter rank					
		1	2	3	4	5	6
SSC	<i>r</i>	0.835	0.868	0.911	0.930	0.909	0.906
	RMSEP	0.353	0.322	0.278	0.259	0.285	0.287
pH	<i>r</i>	0.937	0.938	0.941	0.943	0.930	0.920
	RMSEP	0.085	0.082	0.080	0.076	0.083	0.088

scatter/baseline corrections techniques. SNV was applied to remove the multiplicative interferences of scatter, particle size, and the change in light path (Fig. 3(b)). In standard normal variate correction (SNV), each individual spectrum is normalised to zero mean and unit variance (Nicolaï et al., 2007). MSC was used to compensate for additive (baseline shift) and multiplicative effects in the spectra data which are induced by physical effects. However, the advantage of SNV method over MSC is that SNV is applied to an individual spectrum, whereas MSC uses a reference spectrum such as the mean spectrum of the calibration set. The best smoothing method was the median filter that can be used for spike removal (Fig. 3(c)). Median filter led to better calibration models when compared with the Savitzky–Golay and wavelet filters. Table 4 shows that it is very important to choose the proper median filter rank (i.e. 4 in this study). In addition, the first derivative showed better results than second derivative. As Cen and He (2007) found, the peaks and troughs were not very obvious in the original spectra but became clearer using first derivative (Fig. 3(d)). Fig. 3(e) shows the best combination of pre-processing techniques, i.e. SNV, median filter and first derivative.

3.2. Prediction of internal quality attributes

PLS prediction results for soluble solids content and pH are presented in the scatter plots, Figs. 4 and 5. In both figures, the ordinate and abscissa represent the predicted and measured fitted values of the appropriate parameters, respectively. The

**Fig. 4 – Scatter plots of measured versus predicted SSC using SNV, median filter and first derivative.****Fig. 5 – Scatter plots of measured versus predicted pH using SNV, median filter and first derivative.**

prediction performances of these models were excellent with high correlation coefficient and low RMSEP for each characteristic.

3.2.1. Soluble solids content (SSC)

The best model for the prediction of SSC was developed when SNV, median filter and first derivative were used as pre-processing and a nine-factor PLS model was found to be sufficient for determining the soluble solids content of intact kiwifruit. The correlation coefficient between the measured and the predicted SSC for best model was as high as 0.93, RMSEP of 0.259Brix (Fig. 4).

The values of regression coefficient of SSC obtained in this research were slightly better than those obtained by Shao et al. (2007) with tomato with $r = 0.90$ and $RMSEP = 0.377$; and those obtained by Lu (2001) with the cherries (Sam var.) with $r = 0.89$ and $SEP = 0.65$; by those of Peirs, Lammertyn, Ooms, and Nicolaï (2001) with values between $r = 0.73$ and 0.89 using different apple varieties; by Lammertyn, Nicolaï, Ooms, Smedt, and Baerdemaeker (1998) using apples with $r = 0.82$ and $SEP = 0.6$; by Slaughter, Barrett, and Boersig (1996) using tomatoes with $r = 0.89$ and $SEP = 0.33$; and by Clark et al. (2004) using kiwifruit with $R = 0.92$ and $RMSEP = 0.92\%$. On the other hand Gomez, He, & Pereira, 2006 obtained better results using Satsuma mandarin with $r = 0.94$ and $RMSEP = 0.325\text{Brix}$, and Lu, 2001 also obtained better results in cherries (Hedelfinger var.) with $r = 0.97$ and $SEP = 0.71$. However, the RMSEP achieved in this research ($RMSEP = 0.259\text{Brix}$) was lower than those obtained by others using kiwifruit (e.g. McGlone, Jordan, Seelye, et al., 2002b with $RMSEP = 0.39\%$ and Clark et al. (2004) with $RMSEP = 0.76\%$).

3.2.2. Acidity (pH)

The best model for the prediction of pH was achieved when SNV, median filter and first derivative were used as pre-processing and a nine-factor PLS calibration model was used for determining the pH of intact kiwifruit. The correlation coefficient between the measured and the predicted pH for best model was as high as 0.943, with $RMSEP = 0.076$ (Fig. 5).

The regression coefficients of pH obtained in this study was slightly better to those obtained by Shao et al. (2007) using tomato with $r = 0.83$ and RMSEP = 0.251; by Gomez et al. (2006) in Satsuma mandarin with $r = 0.805$ and RMSEP = 0.179; and by Lammertyn et al. (1998) in apples with $r = 0.93$ and SEP = 0.068.

4. Conclusions

It has been shown that Vis/NIRS is an appropriate tool for prediction of internal quality parameters such as SSC and pH in kiwifruit. Moreover, it was found that Vis/NIRS in combination with chemometrics methods could lead to proper models. It was crucial to choose an appropriate pre-processing method and calibration technique. Calibrations models of transmission mode were improved by the use of more intense light and combination of pre-processing techniques.

The prediction models were developed by principal component analysis (PCA) and partial least square regression (PLS). The effects of different pre-processing techniques were also investigated. Spectral pre-processing techniques were used to remove any irrelevant information that cannot be handled properly by regression techniques. The SNV, median filter and first derivative indicated the best results with high correlation coefficient [$r = 0.93$] and low RMSEP [RMSEP = 0.259] with nine factors for SSC; in the pH model $r = 0.943$ and RMSEP = 0.076 were achieved with nine factors. It was also found that pre-processing methods could affect the accuracy of the NIR calibration models, for instance in the SSC models the correlation coefficient increased by 0.33 and RMSEP was reduced 0.292Brix.

This research showed that VIS/NIRS has a good potential due to its low analysis time and low running cost. It is also possible to develop a non-destructive technique for measuring the internal quality characteristics of fruit. NIRS could become an alternative quality control method in the food industry because of its advantages over other analytical techniques.

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