Nondestructive Determination of Tomato Fruit Quality Characteristics Using Vis/NIR Spectroscopy Technique

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Abstract

The objectives of the study were to evaluate the use of visible/near infrared reflectance spectroscopy (Vis/NIRS) in measuring the quality characteristics of Tomato 'Heatwave' (*Lycopersicum esculentum*), and to establish the relationship between nondestructive Vis/NIR spectra and the major fruit physiological properties, including fruit firmness, soluble solids content (SSC) and acidity (pH). Intact tomato fruit were measured by reflectance (R) in 350–2500 nm range. The absorbance, calculated via log (1/R), was analyzed for the best calibration model of each characteristic, using principal component re-gression (PCR) and partial least square regression (PLS). The results showed excellent prediction performances that the standard error of prediction (SEP) of SSC (r=0.90) was 0.19 ºBrix with three factors; the SEP of pH (r=0.83) was 0.09 with four factors; that of compression force (r=0.81) was 16.017 N with six factors; and that of puncture force (r=0.83) was 1.18 N with three factors. Comparatively, the models had significantly greater accuracy in determining SSC. Thus, the application of the Vis/NIRS measurement technique in the full spectral range (400-2350 nm) could assess the quality characteristics of tomatoes.

Keyword: Vis/NIR spectroscopy, nondestructive technique, tomato quality characteristic, firmness, sugar, acidity.

I. Introduction

In general, fruits are sorted manually or automatically on the basis of size, color, and surface defects such as bruises. However, dry matter content, total soluble solids content, sugar content, juice acidity and firmness are important internal quality attributes of fruit products. Most instrumental techniques to measure these properties are destructive and involve a considerable amount of manual work.
Thus, researches have presently been focused on developing nondestructive techniques, e.g. Visible/NIR spectroscopy, for measuring fruit quality attributes. The visible and near infrared spectroscopy (NIRS) technique use the radiation in the 350-2500 nm wavelength region of the electromagnetic spectrum. It is regarded different from other spectroscopic techniques. Because once the instrument is calibrated, it could be used for days or months without being recalibrated, with limited sample preparation and high speed of analyses. These advantages have been used to affect the analyses of large batches [1].

Nondestructive optical methods based on visible/NIR spectrometry have been evaluated for nondestructive estimation of internal starch, soluble solids content, oil contents, water content, dry matter content, acidity, firmness, stiffness factor and other physiological properties of batches of fruit and vegetable products, such as citruses [2], mandarins [3], fresh tomatoes [4], [5], mangos [6], melons [7], kiwifruits [8], peaches [9], [10], pineapples [11], apples [12], [13]. Differences between sound and damaged tissues in visible and near-infrared diffuse reflectance are useful for detecting bruises, chilling injuries, scalds, decay lesions and numerous other defects. Bruises on apples and peaches can be detected at specific NIR wavelengths; however, the wavelengths chosen for apples differ between fresh and aged bruises because of the drying of the injured tissues [14]. Lu (2001) obtained that the prediction results were slightly better using the multiplicative scatter correction (MSC) as the data pre-processing method and also showed that no single wavelength was strongly correlated with the firmness and sugar content of sweet cherries, which indicated the difficulty of using selected wavebands to predict them accurately [15]. Indistinctly, many researchers have used and established different ranges of wavelength frequency, extending from the visible spectrum to the long longitudes of the NIRS, to estimate multiple fruit properties. But until now no consent has reached on which is the best wavelength range to study each fruit parameter due to different fruit nature, types, characteristics and influences of fruit grow environment.

The objectives of the study were to evaluate the use of Vis/NIR spectroscopy in measuring the quality characteristics of Tomato 'Heatwave' (*Lycopersicum esculentum*), and to establish the relationship between the Vis/NIR spectral measurements and the major physiological properties of tomatoes, including fruit firmness, soluble solids content (SSC) and acidity (pH). Multivariate calibration techniques, such as principal component analysis (PCA), principal component regression (PCR) [16] and partial least squares (PLS) [17], were used for the data statistical analyses and the construction of the prediction models for each fruit quality characteristics.

II. Materials and Methods

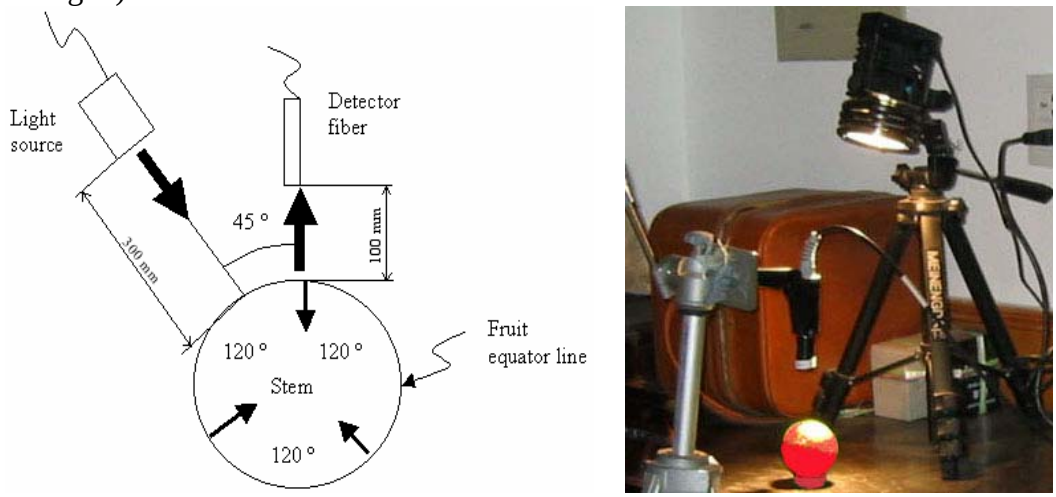
A. *Experimental Procedure and Plant Materials*

Tomato 'Heatwave' (*Lycopersicum esculentum*) was selected for the experiment. All samples were hand harvested from the same simple green house in Hangzhou, China on November 29, 2004. To determine their individual sizes, three measurements at right angles, i.e., two equatorial diameters (at 90 º) and a line from the stem to the fruit blossom end, were taken per fruit with a digital caliper (Mitutoyo 0-150±0.01 mm (UK)). All of these values were averaged accordingly and those of medium size 78±2.5 mm, i.e., a total of 200 tomatoes, were selected based on their color uniformity (between pink and light red) and sizes. Each sample (fruit) was individually numbered. As the fruits were harvested from different trees, the experiment design was completely randomized with each fruit as an experimental unit.

B. *Reflectance Measurement Analysis*

Three reflection spectra (350–2500 nm) were taken at three equidistant positions around the equator (approximately 120 º) of each tomato with a spectrophotometer (FieldSpec Pro FR (350–2500 nm)/A110070, Analytical Spectral Devices, Inc. (ASD)), using the RS2 software for Windows® (see Fig. 1). For each reflectance spectrum, the scan number was set 10 at exactly the same position. Thus, the total scan number for each example was 30. After all spectral measurements were completed, the acquired data were properly stored for later use.

The light source consisted of a Lowell pro-lam interior light source (Assemble/128930) with the Lowell pro-lam 14.5 V Bulb/128690 tungsten halogen that could be used both in the visible and near infrared regions. The light source was placed at a distance of 300 mm from the fruit surface (see Fig. 1). With the bifurcated optical configuration, the light was guided to the sample by the source fibers and received from the sample by the detector fibers. The angle between the incident light (light source) and the detector fiber (pistol grip unit 6307) was 45 º (see Fig. 1). The fibers had a 4 mm2 active surface with an 8 º obliquity angle, and were placed at the height of 100 mm from the fruit surface (see Fig. 1).



(a) (b)

Fig. 1. Vis/NIRS experimental instrument setup for each tomato ((a) the positions of the light source and the detector fiber from the sample fruit and the three equidistant angels around the equator of each tomato; (b) the platform for optical reflectance measurement of tomatoes)

The reflected light was divided into individual wavelengths by the diffracting gratings of the monochromator. Grating A was used for the wavelength range 350–1000 nm and grating B for 1000–2500 nm. A 512 element NMOS photodiode array was used for the visible and the beginning of the near infrared ranges (300–1100 nm) with 1.4 nm sampling interval; and another two separate thermoelectrically cooled “graded index” InGaAs photodiodes were used in the NIRS range (1000–2500 nm) with 2 nm sampling interval.

A 100 mm^2 Teflon® disk was used as the optical reference standard for the system, since Teflon had low reflectance and its light-scattering characteristics were similar to those of the samples. The reflectance (R) was calculated by comparing the near infrared energy reflected from the sample with the standard reference.

Each spectrum measurement, including that of the Teflon standard measured prior to each reflection spectra, were recorded as an average of 30 scans. The signals were pre-processed in the software ViewSpec Pro V2.14 (Analytical Spectral Device, Inc. 5335 Sterling Drive Suite A, Boulder, CO 80301). For each fruit, a mean spectrum was calculated by total scan spectra averaging collected at the three positions around the fruit equator. Fig. 2 shows the average spectra reflectance (R) for one tomato. Due to the imperfection of the system and the negative influences from the environmental light, a big scattering could be observed at the beginning and end of the spectral data. Considering their affecting the measurement accuracy, the first 50 and the last 150 wavelength values were eliminated for all analyses. Thus, all consideration was based on the wavelength range of 400-2350 nm.

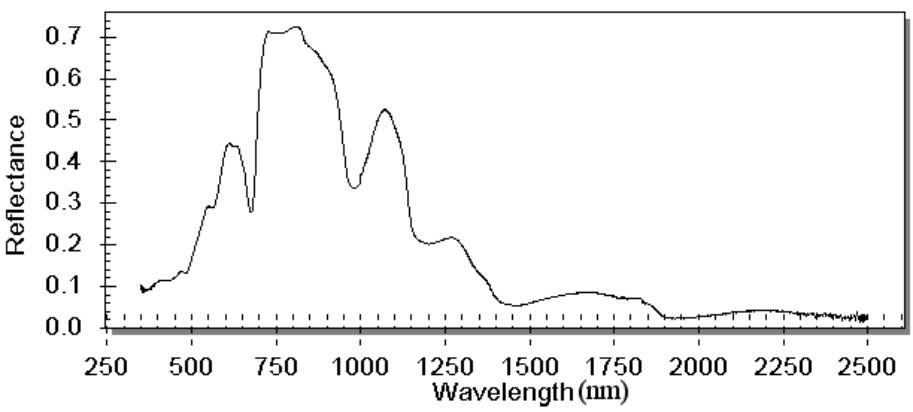


Fig. 2. Original reflectance spectra for one tomato (350-2500 nm) (mean value of 30 scans)

C. *Other measurements*

In order to assess the real quality characteristics of fruit at harvest time, the fruit firmness by Magness-Taylor puncture and compression tests, soluble solids content (SSC) and acidity (pH) were determined.

In the compression tests, the fruit firmness was quantified by the maximum compression force (Fc), which was required to compress the fruit by 3% of its diameter and recoded at a strain rate of 0.00016 m/s (10 mm/min). The maximum compression forces of all fruit individuals were measured on the three specific positions along the equator, with approximately 120 º between them and perpendicular to the stem-bottom axis. The measurements were carried out on the Universal Testing Machine (Model 5543 Single Column, Instron Corp., Canton MA. USA), using parallel plates for the compression tests.

In the Magness-Taylor puncture tests, the fruit was supported by a cradle of 75 mm diameter (about the same as the fruit) with hemispherical depression in the center of an aluminum plate. In this test, a cylindrical plunger (6 mm diameter) was punctured in the fruit. The data were plotted using a trip recorder at 5 kgf full scales. The crosshead speed was 0.00016 m/s (10 mm/min). The forces of all fruit individuals were also measured on the three positions along the fruit equator, perpendicular to the stem-bottom axis, with approximately 120 º between them. And a 500 N load cell was used for firmness determination. This test measured the individual fruit firmness based on its resistance to penetration by the probe. The peak of penetrating force required to cause fruit rupture, i.e., the maximum puncture force (F), was measured. The reference measurement in all cases was 0.05 N.

The pH and soluble solids content (SSC) of the juice samples were determined after compression and puncture tests, using the pH meter (model 320-s) manufactured by Mettler Toledo Scale Company Shanghai corp., Switzerland and the digital refractometer WYT-J 0-32 ºBrix, Beijing, China, respectively. All of these measurements were performed immediately after Vis/NIRS measurements.

D. *Optical Data Processing*

To test the influences of the preprocessing methods on the prediction of the calibration models, two types of pretreatment were used. The first one was to smooth using moving average, i.e., to decrease the wavelength resolution of the spectra (1.4 and 2 nm for spectral ranges 350-1000 nm and 1000–

2500 nm, respectively) n times for n subsequent wavelengths by averaging the reflectance values. Thus, was reduced n times, resulting in a decrease of resolution of n times, respectively. As a result, the number of the measurement points of each spectral curve was reduced by 5, 9, 13, 17, 21 and 27 times, respectively. And prediction results of the further multivariate calibration based on the different smoothing factors were compared with each other and the most appropriate averaging segment size was selected to establish the best models for each tomato quality parameter.

The other pre-processing was multiplicative scatter correction (MSC), which was used to correct additive and multiplicative effects in the spectra [18]. Due to the fruit fresh light scattering, the light did not always travel the same distance from the sample when being detected. A longer light traveling path corresponded to lower relative reflectance values, since more light was absorbed. The phenomenon would cause a parallel translation of the spectra. However, this kind of variation was of no use for the calibration models and could be eliminated by MSC.

All fruit reflectance measurements were transformed to absorbance ((log (1/R)) values for linearizing the correlation of the NIR values with the concentration of estimated constituents. The processed data were combined with the above four quality parameters for the statistical analysis in 'Unscrambler V8.0.5 1986-2003 (CAMO, PROCESS, AS, OSLO, Norway), a statistical software package for multivariate calibration.

Before calibration, the spectra variation was analyzed by principal component analysis (PCA) to eliminate the defective spectral outliers. Principal component regression (PCR) and partial least squares (PLS) [17] were combined to build the prediction models. Contrarily, the multilinear regression (MLR) was not recommended for the collinearity between the adjacent wavelengths [13], because PLS and PCR described the original data more efficiently as they were transformed into a set of orthogonal variables.

The sample data (200 tomatoes) were separated randomly into two groups: the calibration set (170 fruit) for developing the calibration models and the remaining samples of the population (30 fruit) were utilized as the prediction set. Besides, the calibration models were validated by the full cross validation.

III. Results and Discussion

A. Selection of the Best Models

For each fruit quality of interest, different calibration models were calculated depending on the results of PCR or PLS. The spectra pre-processing and the number of factors (latent variables) were both taken into consideration. Therefore, the following two criteria were considered to select the most desirable model for each tomato physiological characteristics.

First, the quality of the calibration model is quantified by the standard error of calibration (SEC), the standard error of prediction (SEP) and the correlation coefficient (r) between the predicted and the measured parameters. Thus, good models should have lower SEC and SEP, higher correlation coefficients but smaller differences between SEC and SEP, because large differences indicate that too many latent variables are introduced in the model and the noises are also modeled. SEC and SEP are respectively defined as:

$$\mathrm{SEP} = \sqrt{\frac{1}{I_p - 1}\sum_{i=1}^{I_p}(\hat{y}_i - y_i - bias)^2} \quad (1)$$

$$\mathrm{SEC} = \sqrt{\frac{1}{I_c - 1}\sum_{i=1}^{I_c}(\hat{y}_i - y_i)^2} \quad (2)$$

Where $\hat{y}_i$ is the predicted value of each observation and y_i is the measured value; I_c is the observation number in the calibration set and I_p is the observation number in the validation set; and bias is the systematic differences between the predicted and the measured. It could be calculated via:

$$\mathrm{bias} = \frac{1}{I_p}\sum_{i=1}^{I_p}(\hat{y}_i - y_i) \quad (3)$$

Second, a relative low number of latent variables (LV) are generally desirable to avoid the modeling signal noises. The minimum plot of the root mean squared error of prediction (RMSEP) of the parameters in question against the number of latent variables was used to determine the optimal amount of latent variables. The correct number of regression factors for the PLS and PCR models was determined according to the minimum root mean square error of cross validation. More variables would result in "overfitted" models, while fewer would produce "underfitted" ones. The RMSEP is defined as:

$$\mathrm{RMSEP} = \frac{1}{I_p}\sum_{i=1}^{I_p}(\hat{y}_i - y_i)^2 \quad (4)$$

After several different pretreatment to choose the best model for each quality characteristics using methods of PLS and PCR, the results to each analyzed parameter were summarized in Table 1.

Table 1. Results of calibration and full cross validation of the best models by PLS and PCR (spectrum range 400-2350 nm)

Parameter	Gapsize	Method	Calibration				Cross-validation		
			LV	*r*	SEC	RMSEC	*r*	SEP	RMSEP
SSC	13	PLS	3	0.95	0.11	0.11	0.91	0.01	0.16
	13	PCR	5	0.92	0.14	0.14	0.86	0.19	0.19
pH	9	PLS	4	0.92	0.07	0.07	0.85	0.08	0.09
	9	PCR	7	0.90	0.07	0.07	0.83	0.09	0.09
Fc	13	PLS	6	0.88	1.19	1.17	0.81	1.50	1.48
	17	PCR	7	0.87	1.21	1.2	0.82	1.45	1.43
F	21	PLS	3	0.92	0.79	0.78	0.87	0.98	0.97

17	PCR	5	0.91	0.83	0.82	0.87	1.00	0.99

It could be concluded from the above table that the calibration methods influenced the results as well. The PLS models were lightly better than the PCR ones. This was explained by the fact that the PLS models did not include the latent variables that were less important to describe the variance of the quality parameter. Consequently, they would always have the lowest number of variables [19]. Moreover, it should be noted that PCR and PLS both had the potential to estimate not only the component concentrations but chemical and physical properties from the infrared spectra. On the other hand, these results agreed with the conclusions made by Haalan et al. (1988) [17], as well as those obtained by Lammertyn et al. (1998) who adopted similar approaches to choose the best model for prediction of apple quality characteristics [13]. Table 2 showed the summary statistics for all samples selected in each data set. When building the calibration model for each parameter, some measurements (samples) were taken out, i.e., 2, 1 and 1 for SSC, compression and puncture forces, respectively, due to their potential bad influences over the models, which was indicated during PCA pre-analysis.

Table 2. Statistical analysis of the analytical, calibration, validation and prediction sample sets, i.e., the data ranges, means and standard deviation (S.D)

Characteristic	Item	Analytical		Calibration	Validation	Prediction
SSC (^{o} Brix)	NO.	*100*	*30*	*98*	*98*	*30*
	Range	3.14-4.41	2.14-4.54	3.19-4.36	3.19-4.45	2.26-4.3
	Mean	3.843	3.482	3.844	3.857	3.459
	S.D	0.37	0.73	0.354	0.349	0.708
pH	NO.	*100*	*30*	*100*	*100*	*30*
	Range	4.08-4.86	4.03-4.77	4.08-4.74	4.07-4.76	4.04-4.78
	Mean	4.36	4.428	4.361	4.354	4.446
	S.D	0.169	0.212	0.155	0.154	0.206
Fc (N)	NO.	*100*	*30*	*99*	*99*	*30*
	Range	6.71-15.32	7.94-85.6	6.43-15.03	5.71-14.87	4.60-73.65
	Mean	10.56	39.021	10.562	10.555	37.738
	S.D	2.503	27.665	2.203	2.230	25.005
F (N)	NO.	*100*	*30*	*99*	*99*	*30*
	Range	2.58-9.8	5.64-28.94	2.99-9.01	2.96-9.39	5.75-24.70

Mean	6.14	13.74	6.142	6.169	13.707
S.D	2	7.876	1.844	1.801	7.034

B. *Prediction of Individual Quality Characteristics*

PLS prediction results for soluble solids content, acidity, compression and puncture forces are presented in the scatter plots shown in Fig. 3. In all figures, the ordinate and abscissa axes respectively represent the predicted and measured fitted values of the corresponding parameters. The correlation between them for each characteristic implied if the established prediction models were reasonable and if the prediction performances of the models were excellent.

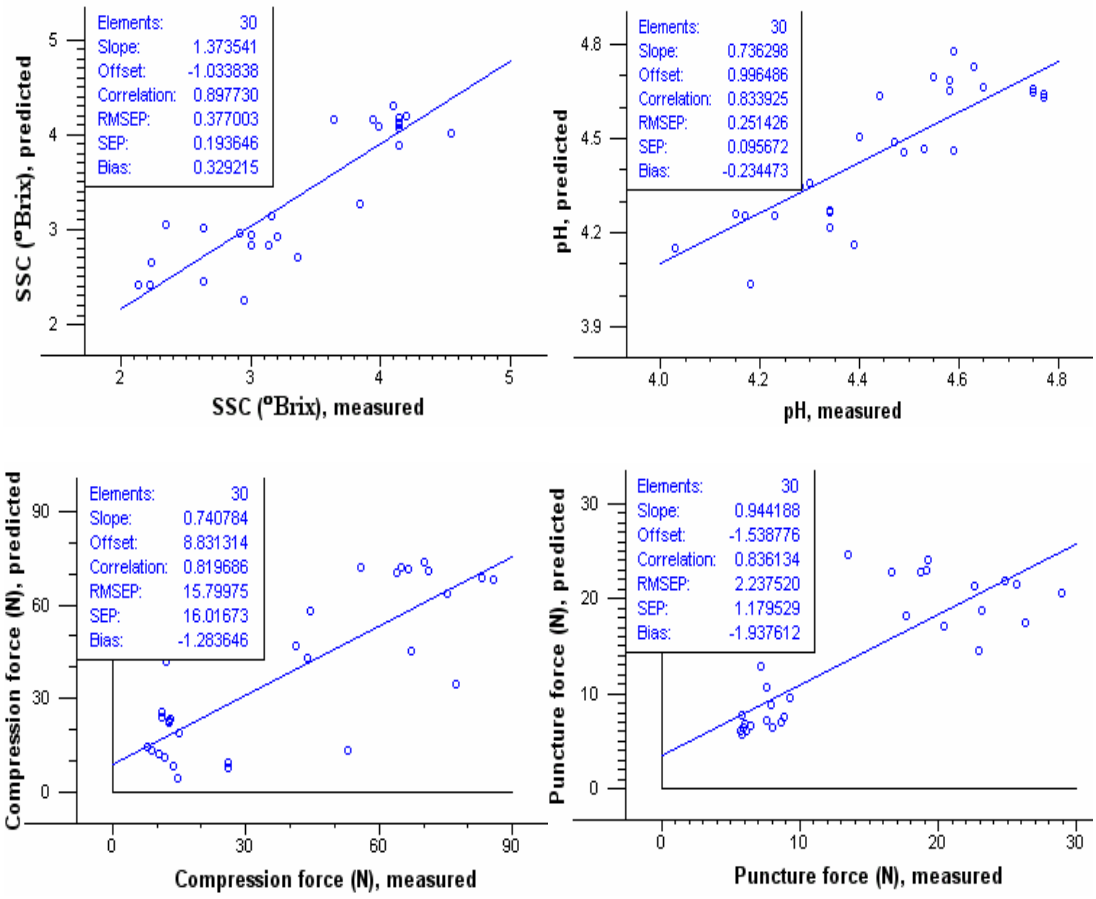


Fig. 3. Vis/NIRS prediction results of the established PLS models for each tomato physiological parameter, including soluble solids content (SSC), acidity (pH), compression force (Fc) and puncture forces (F)

C. *Soluble Solids Content (SSC)*

The calibration correlation between the NIR measurements and the SSC was as high as 0.95, with the standard error of calibration (SEC) 0.11 ºBrix (see Table 1). When the model was used to predict the other 30 samples, the prediction results were also desirable, with the correlation coefficient between the measured and the predicted (*r*) 0.90, the standard error of prediction (SEP) 0.19 ºBrix

with a bias 0.33 ºBrix (see Fig. 3). The PLS model appeared to be robust since only three factors (LVs) were used in the calibration model (see Table 1).

The regression coefficients of SSC obtained in this research were lightly superior to those obtained by Lammretyn et al. (1998) in apples with *r*=0.82 and SEP=0.61 [13]; by Peirs in different apples varieties (2000) with *r*=0.73–0.89 [20]; by Slaughter et al. (1996) in tomatoes with *r*=0.89 and SEP=0.33 [4]; and by Lu (2001) in the cherries Sam variety with *r*=0.89 and SEP=0.65 [21]. However, better results had been achieved in cherries Hedelfinger variety with *r*=0.97 and SEP=0.71 by Lu (2001) [21]; mandarins with *r*=0.989 and SEP=0.32 by Kawano et al. (1992) [22]. Osborne and Künnemeyer (1999) and McGlone et al. (2003) had studied the kiwifruits and mandarins and obtained respectively the results with RMSEP=0.27 ºBrix and RMSEP=0.32 ºBrix [8], [3], which were both minor than 0.38 ºBrix in this paper (see Table 1) that was in turn smaller than the one RMSEP=0.5 ºBrix achieved in apples by McGlone et al. (2002) [23]. Peiris et al. (1997, 1998) obtained in peaches *r*=0.57 and SEP=0.74% using PLS validation [5], [9]. And for comparison with PLS, they also adopted neural networks and the results turned out to be better with bias=-0.03%, SEP=0.52% and *r*=0.69. However, both the above prediction results could be considered poor.

D. Acidity (pH)

The calibration correlation between the NIR measurements and the pH of tomatoes was adequately high, with *r*=0.92 and SEC=0.07 (see Table 1). When the calibrated model was applied to the prediction set (30 samples), the results were applicable with *r*=0.83, SEP=0.096 and bias=–0.234 (see Fig. 3). The PLS model appeared to be acceptable since four factors (LVs) were used in the calibration model (see Table 1). Lammretyn et al. (1998) obtained in apples a regression coefficient (*r*) 0.93 and SEP=0.068, both of which were superior to the results in this research [13].

E. Compression Force (Fc)

In the case of compression force, a good regression coefficient was obtained in the calibration set, with *r*=0.88 and SEC=1.18 N (see Table 1). When the model was used to predict the remaining 30 samples, the results were *r*=0.81, SEP=16.017 N and bias=-1.284 N (see Fig. 3). The PLS model appeared to be acceptable due to the six factors (LVs) used in the calibration model (see Table 1). In spite of the good correlation between the predicted and the measured compression forces, the relatively high SEP=16.017 N might be the result of the larger standard deviation (S.D) of the prediction data set 27.665 N (see Table 2). In literature, little information was found concerning NIR spectroscopy prediction models for compression force of 3% fruit high equator.

F. Puncture Force (F)

The calibration correlation between the NIR measurements and the puncture forces was good, with *r*=0.92 and SEC=0.79 N (see Table 1). When the model was used to predict the remaining 30 samples, reasonable results were obtained, with *r*=0.84, SEP=1.18 N, bias=-1.938 N (see Fig. 3). And three factors (LVs) were used in the calibration model (see Table 1).

The regression coefficients obtained in the puncture force were superior to those obtained by Lammretyn et al. (1998) in apples with a poor correlation coefficient (r) from 0.73 to 0.75 [13], and by Lu (2001) in cherries Sam variety with *r*=0.65 and SEP=0.44 N and similarly in cherries Hedelfinger variety with *r*=0.80 and SEP=0.55 N [21]. The RMSEP=2.24 N was also superior to those reported in the Vis/NIRS literature on apples: RMSEP=7.5 N in McGlone et al (2002) [12].

In the above discussion of the PLS prediction results, no consideration was given to the contributions of the individual wavelengths to the prediction results. This was because the PLS method first applied linear transform to the entire individual wavelength data. As a result, it was often difficult to ascertain how individual wavelengths were directly related to the quantities to be predicted. However, it would be helpful to examine how sugar content, acidity or firmness were simply related to individual wavelengths so that a better understanding their correlated NIRS might be achieved.

IV. Conclusions

The advantages of NIR spectroscopy were obvious: it was a feasibly quick and nondestructive technique for measurement and the quality characteristics could be measured repeatedly for the same sample. The results in this paper indicated that it was possible to utilize this nondestructive technique to measure tomato quality characteristics. The multivariate calibration methods PCR and PLS both had the potential to estimate the component concentrations, the chemical and physical properties of the tomatoes from their infrared spectra.

By means of PLS, a correlation was established between the absorbance spectra and the quality parameters of tomatoes. In the SSC model, r=0.90 and SEP=0.19 ºBrix with three factors; in the pH model, r=0.83 and SEP=0.09 with four factors; in the compression force model, r=0.81 and SEP=16.017 N with six factors, and in the puncture force model r=0.83 and SEP=1.18 N with three factors. All results showed excellent prediction performances of the established PLS models for each tomato quality characteristics. Comparatively, the Vis/NIR spectroscopy technique had significantly greater accuracy during the determination of SSC.

As to the data preprocessing methods, they influenced the prediction performances of the models. In general, the models based on spectra preprocessed by MSC performed slightly better than those without MSC. For the other spectral data pretreatment, i.e., smoothing by moving average, the different segment size (5, 9, 13, 17, 21 and 27 times) applied during the initial spectral pretreatment in this paper had light influences on the established prediction models.

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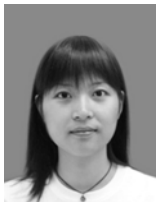

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