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Determination of soluble solid content and acidity of loquats based on FT-NIR spectroscopy*

Xia-ping FU, Jian-ping LI†‡, Ying ZHOU, Yi-bin YING, Li-juan XIE,
Xiao-ying NIU, Zhan-ke YAN, Hai-yan YU

(*College of Biosystem Engineering and Food Science, Zhejiang University, Hangzhou 310029, China*)

†E-mail: jpli@zju.edu.cn

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Abstract: The near infrared (NIR) spectroscopy technique has been applied in many fields because of its advantages of simple preparation, fast response, and non-destructiveness. We investigated the potential of NIR spectroscopy in diffuse reflectance mode for determining the soluble solid content (SSC) and acidity (pH) of intact loquats. Two cultivars of loquats (Dahongpao and Jiajiaozhong) harvested from two orchards (Tangxi and Chun'an, Zhejiang, China) were used for the measurement of NIR spectra between 800 and 2500 nm. A total of 400 loquats (100 samples of each cultivar from each orchard) were used in this study. Relationships between NIR spectra and SSC and acidity of loquats were evaluated using partial least square (PLS) method. Spectra preprocessing options included the first and second derivatives, multiple scatter correction (MSC), and the standard normal variate (SNV). Three separate spectral windows identified as full NIR (800~2500 nm), short NIR (800~1100 nm), and long NIR (1100~2500 nm) were studied in factorial combination with the preprocessing options. The models gave relatively good predictions of the SSC of loquats, with root mean square error of prediction (RMSEP) values of 1.21, 1.00, 0.965, and 1.16 °Brix for Tangxi-Dahongpao, Tangxi-Jiajiaozhong, Chun'an-Dahongpao, and Chun'an-Jiajiaozhong, respectively. The acidity prediction was not satisfactory, with the RMSEP of 0.382, 0.194, 0.388, and 0.361 for the above four loquats, respectively. The results indicate that NIR diffuse reflectance spectroscopy can be used to predict the SSC and acidity of loquat fruit.

Key words: Near infrared (NIR) spectroscopy, Loquats, Soluble solid content (SSC), Acidity, Partial least square (PLS), Modeling, Spectra preprocessing

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INTRODUCTION

Fruit internal quality is an important factor influencing marketing transportation and storage requirements. Determination of fruit internal quality using destructive and invasive methods such as chemical or texture analysis is more complicated than external quality detection (like shape, color, size, etc.) (Hsieh and Lee, 2005). It is impossible to apply these methods for on-line assessment. Near infrared (NIR) technique is a fast and nondestructive approach, which can obtain internal information of a product by measuring the amount of light absorbed by functional groups over the NIR spectral range without or with little sample preparation.

NIR region was first discovered by Herschel (1800) as early as 1800; however, it had been ignored for 50 years in the first half of the 19th century. Although the earliest applications of NIR spectroscopy for agricultural and food samples were reported in the 1950s by the group headed by Norris (Mercurl *et al*., 1957), it was not until 1970s that NIR analyzers were developed. From the later 1980s, NIR spectroscopy has gained wide acceptance by its advantages over other analytical techniques and has been used in various fields. By now, many studies have reported that NIR spectroscopy techniques can

‡ Corresponding author

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nondestructively detect internal qualities, such as soluble solid content (SSC), valid acidity, dry matter, and firmness of fruit. For example, Ventura *et al*. (1998) used NIR method (at 810~999 nm) based on a dual-beam, fiber-optic portable spectrometer to determine SSC in Golden Delicious and Jonagold apples nondestructively. They used multiple linear regression (MLR) models for prediction and obtained standard error of prediction (SEP) of 1.14 °Brix. Lammertyn *et al*.(2000) established the relationship between the reflectance spectra (at 880~1650 nm) and the SSC of apples by means of the partial least square (PLS) technique. Lu and Ariana (2002) investigated an NIR sensing technique in interactant mode for rapid acquisition of spectral information to predict the sugar content and possibly firmness of Empire and Red Delicious apples. Others (Kawano *et al*., 1993; Slaughter, 1995; Peiris *et al*., 1999; McGlone *et al*., 2002; Ying *et al*., 2005; Liu and Ying, 2005; Liu *et al*., 2007; Ariana *et al*., 2006; Fu *et al*., 2008) have studied other fruits, such as cucumbers, mandarins, kiwifruits, peaches, and pears, based on NIR spectroscopy technique.

Loquat (*Eriobotrya japonica* Lindl) has been cultivated in China for more than 2000 years and now is mainly planted in Zhejiang, Fujian and Jiangsu Provinces. Different varieties have different shape, color, size, etc. For loquats, external defect and size were two main parameters used for classifying by farmers. However, it is difficult for them to evaluate the internal quality. SSC and acidity are two important factors that affect loquat quality and strongly influence its taste and market value. It is important to develop a nondestructive approach to measure these qualities for loquat quality control and classification. So far, no studies have been reported on using NIR techniques for measuring the SSC and acidity of loquats.

The objective of this research was to investigate the potential of NIR spectroscopy in diffuse reflectance mode for determining the SSC and acidity (pH) of intact loquats. We also examined the influence of spectra preprocessing, such as derivative, multiple scatter correction (MSC), and standard normal variate, on NIR modeling performance for SSC and acidity prediction in three wavelength regions: full NIR region (800~2500 nm), short NIR region (800~1100 nm), and long NIR region (1100~2500 nm).

MATERIALS AND METHODS

Loquat samples

Mature Dahongpao and Jiajiaozhong loquats were harvested from two commercial orchards in Tangxi and Chun'an, two of the main loquat production areas in Zhejiang Province, China. A total of 400 loquats (100 samples of each cultivar from each orchard) were manually picked during commercial harvest period, transported immediately to the laboratory, and stored in a cooler (4 °C) for study. Before test, samples of one cultivar from one orchard were taken out from the cooler and maintained at room temperature (25 °C) for 24 h to equilibrate to the experimental condition. The measurements including spectra collection and quality analysis of these samples were carried out on the same day.

Spectral data acquisition

NIR spectra of intact loquats were acquired in diffuse reflectance mode. A custom-designed laboratory system was utilized, which consisted of a fruit holder/light collection fixture, a Fourier transform infrared (FT-IR) spectrometer (Thermo Electron Corp., Madison, Wisc., USA), a bifurcated optical fiber, and a computer. The fiber optic probe was enclosed in a 16-mm-diameter stainless steel cylindrical tube, with both light source beams and receptor beams enclosed in it randomly. The spectrometer had a wide band light source (50 W quartz tungsten halogen lamp), an interferometer, and a thermal electric cooled InGaAs detector with a spectral range of 800~2630 nm. Spectral data acquisition and storage were achieved with the computer running software OMNIC v6.0 (Thermo Electron Corp., Madison, Wisconsin, USA). Each reflectance spectrum was accumulated by averaging 64 repetitive scans at a single location with resolution of 16 cm^{-1} and then transformed to absorption $\log(1/R)$, where R is the ratio of light intensity reflected from the fruit to light intensity reflected from the Teflon block. Loquats were positioned centrally and steadily upon the fruit holder, with stem-calyx axis horizontally oriented. For each fruit, three locations were selected around the equator (about 120° apart). Before sample spectra collection, the standard reference spectrum was obtained by placing a Teflon block on the fruit holder and measuring the intensity of reflected light.

SSC and acidity measurement

According to the China Standard (1990) for SSC measurement in fruit, the flesh of each fruit (by removing the peel and stone) was used for extracting juice with a commercial juice extractor. Filtered supernatant juice was used for determination of SSC and acidity. SSC was measured by a digital refractometer (ATAGO PR-101, Tokyo, Japan). Following the China Standard (1989) for valid acidity measurement in fruit, acidity was detected by a pH meter (SJ-4A, Exact Instrumentation Co., Shanghai, China).

Data processing and analysis

NIR calibration and validation were conducted using a random split of the fruit of each variety: a calibration set (70 samples) and a validation set (30 samples). The principal modeling tool used was the PLS method (TQ Analyst v6.1, Thermo Electron Corp., Madison, Wisconsin, USA). Spectra preprocessing options included the first and second derivatives, MSC, and the standard normal variate (SNV). Three separate spectral windows identified as full NIR (800~2500 nm), short NIR (800~1100 nm), and long NIR (1100~2500 nm) were studied in factorial combination with the preprocessing options. The optimal combination was chosen on the basis of the minimum root mean square error of cross validation (RMSECV), which was also used to choose the number of factors in the model, up to a maximum of 20. Once completed, the calibration model was applied to the validation set, and the regression analysis between actual SSC/acidity and predicted SSC/acidity was used to judge the predictive performance of the model using the statistic correlation coefficient R and the root mean square error of prediction (RMSEP).

RESULTS AND DISCUSSION

SSC and acidity of samples

Table 1 summarizes the maximum, minimum, means and standard deviations of four datasets (two varieties from two orchards: Tangxi-Dahongpao, Tangxi-Jiajiaozhong, Chun'an-Dahongpao, and Chun'an-Jiajiaozhong). On average, Dahongpao loquats were much sweeter and less sour (higher pH value) than Jiajiaozhong, as indicated by the average SSC and acidity. Dahongpao loquats had more variations in both SSC and acidity than Jiajiaozhong did. As shown in Table 1, Chun'an-Dahongpao loquats had the highest SSC and pH value (SSC=15.06 °Brix, pH=4.59), Chun'an-Jiajiaozhong had the lowest SSC (10.80 °Brix), and Tangxi-Jiajiaozhong had lowest pH (3.61).

Spectra of samples

Four spectra corresponding to the four datasets are shown in Fig.1. Each spectrum was the average of 100 spectra in each dataset. The diffuse reflectance spectra curves were quite smooth across the entire

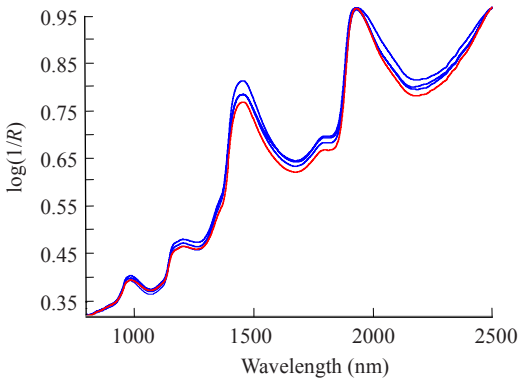

Fig.1 Average diffuse reflectance spectra of four datasets

Table 1 Statistics of SSC and acidity for each dataset

Dataset	SSC (°Brix)				Acidity (pH)			
	Maximum	Minimum	Average	*SD*	Maximum	Minimum	Average	*SD*
Tangxi-Dahongpao	19.80	5.70	14.07	2.61	5.07	3.22	4.32	0.41
Tangxi-Jiajiaozhong	17.40	8.40	12.79	1.65	4.26	3.21	3.61	0.18
Chun'an-Dahongpao	20.10	9.20	15.06	2.10	5.44	3.43	4.59	0.43
Chun'an-Jiajiaozhong	16.80	6.50	10.80	2.09	5.29	3.24	4.33	0.36

SD: standard deviation

NIR spectral region and were characterized by five broad absorption peaks. Absorption band at 1940 nm is related to combination band of water. Absorption bands around 1450 nm and 970 nm are related to the O−H first and second overtones of water, respectively. And bands at 1790 nm and 1190 nm are related to the C−H second and third overtones.

SSC predictions

The preprocessing of the diffuse reflectance spectra, including derivatives, MSC and SNV correction, and the number of factors (from 1 to 20) with PLS models were taken into account. The performance of the models was evaluated by leave-one-out cross validation, that is, the minimum RMSECV and maximum correlation coefficient of cross validation (R_{cv}). The RMSECV with different number of factors of PLS quantitative models for SSC prediction is shown in Fig.2. For each dataset, the RMSECV decreased with an increasing number of factors until it reached a certain number. The optimum number of calibration factors was selected based on the minimum RMSECV. The results of models based on original spectra in full wavelength range (800~2500 nm) were always better than those of models based on derivative spectra (the 1st derivative and 2nd derivative spectra) in short NIR (800~1100 nm) and long NIR (1100~2500 nm). The calibration, cross validation, and prediction results of SSC from the PLS models for Dahongpao and Jiajiaozhong loquats from two orchards are shown in Fig.3 and Table 2. The modeling results were better based on original spectra compared with those based on spectra after MSC and SNV correction, except for Tangxi-Jiajiaozhong variety.

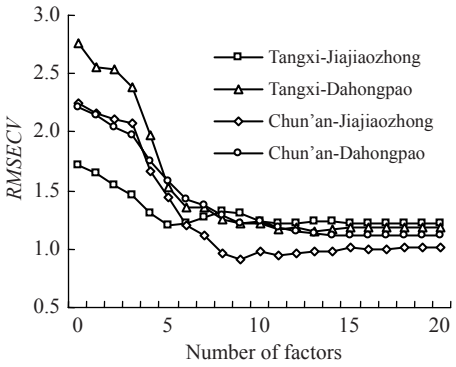

Fig.2 RMSECV with different number of factors of PLS quantitative models for SSC prediction

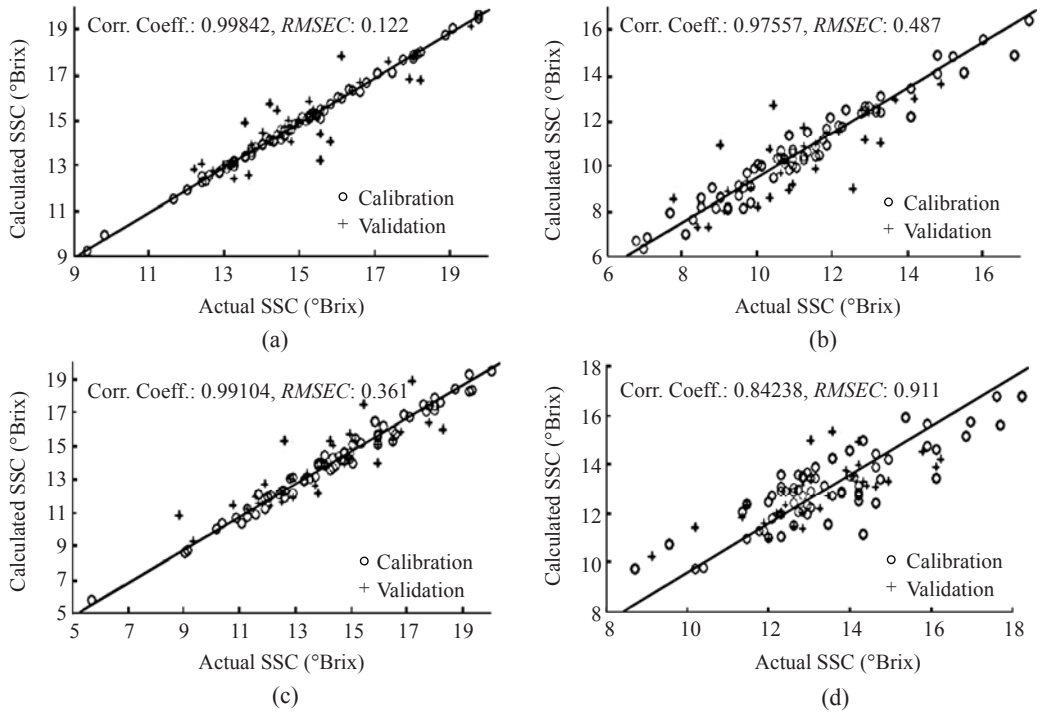

Fig. 3 PLS calibration results for SSC of four datasets
(a) Chun'an-Dahongpao; (b) Chun'an-Jiajiaozhong; (c) Tangxi-Dahongpao; (d) Tangxi-Jiajiaozhong

Table 2 Cross validation and prediction statistics for SSC predictions of four datasets

Sample sets	Preprocessing	N_F	Cross validation			Prediction	
			N_c	*RMSECV*	R_{cv}	N_p	*RMSEP*
Tangxi-Dahongpao	—	11	70	1.180	0.901	30	1.210
Tangxi-Jiajiaozhong	MSC	5	70	1.180	0.717	30	1.000
Chun'an-Dahongpao	—	14	70	1.110	0.860	30	0.965
Chun'an-Jiajiaozhong	—	9	70	0.923	0.909	30	1.160

Abbreviations are number of samples in the calibration (N_c) and prediction (N_p) sets, number of factors (N_F) used, root mean square error of cross validation (*RMSECV*) and prediction (*RMSEP*), and correlation coefficient of cross validation (R_{cv})

The correlation coefficient and RMSEC of PLS calibration models for SSC of Tangxi-Dahongpao, Tangxi-Jiajiaozhong, Chun'an-Dahongpao, and Chun'an-Jiajiaozhong were 0.991, 0.361; 0.842, 0.911; 0.998, 0.122; and 0.976, 0.487, respectively (Fig.3). According to cross validation (Table 2), the model for Chun'an-Jiajiaozhong obtained the best results, with R_{cv}=0.909, and the model for Tangxi-jiajiaozhong was the worst, with R_{cv}=0.717.

Acidity predictions

The same methods were applied to acidity prediction. The calibration, cross validation, and prediction results of acidity from the PLS models for Dahongpao and Jiajiaozhong loquats from two orchards are shown in Fig.4 and Table 3. Original spectra in full wavelength range (800~2500 nm) were also better for modeling than derivative spectra (the 1st derivative and 2nd derivative spectra) in short NIR (800~1100 nm) and long NIR (1100~2500 nm). The modeling results were better based on spectra after MSC (Tangxi-Jiajiaozhong, Chun'an-Dahongpao and Chun'an-Jiajiaozhong) and SNV (Tangxi-Dahongpao) correction compared with those based on original spectra.

The correlation coefficient and RMSEC of PLS calibration models for acidity of Tangxi-Dahongpao, Tangxi-Jiajiaozhong, Chun'an-Dahongpao, and Chun'an-Jiajiaozhong were 0.820, 0.237; 0.809, 0.099; 0.531, 0.367; and 0.687, 0.273, respectively (Fig.4). According to cross validation (Table 3), the model for Tangxi-Jiajiaozhong obtained the best results, with R_{cv}=0.609; and the model for Chun'an-Dahongpao was the worst, with R_{cv}=0.374. The model results for acidity prediction were much worse than those for SSC prediction.

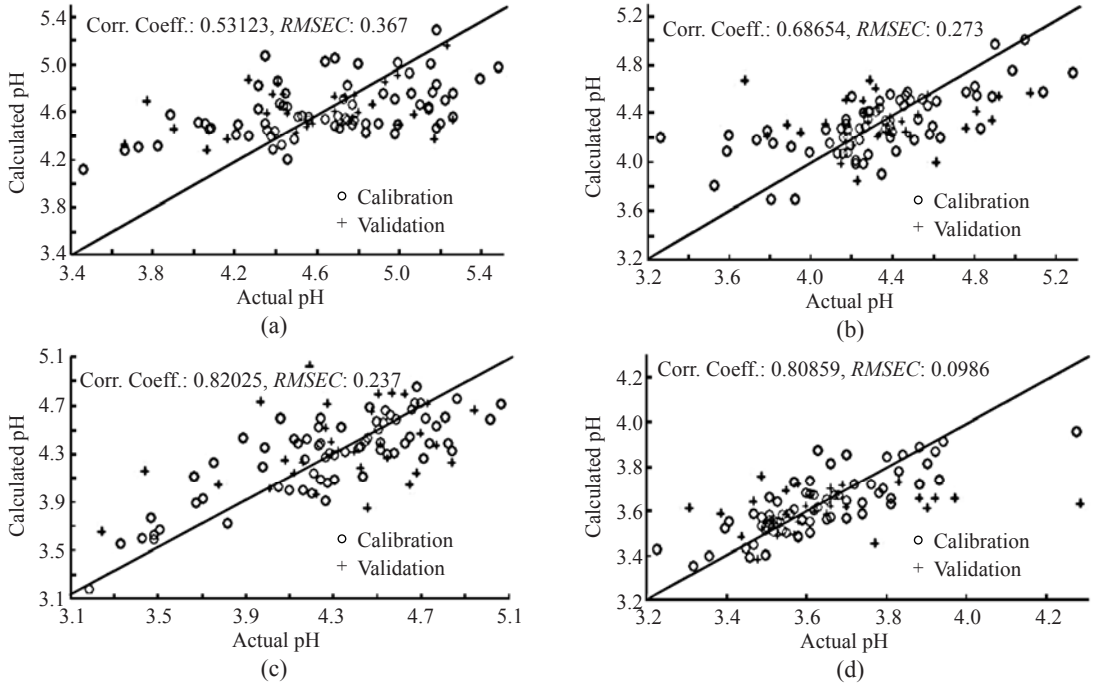

Fig.4 PLS calibration results for acidity of four datasets
(a) Chun'an-Dahongpao; (b) Chun'an-Jiajiaozhong; (c) Tangxi-Dahongpao; (d) Tangxi-Jiajiaozhong

Table 3 Calibration and validation statistics for acidity predictions of four datasets

Sample sets	Preprocessing	N_F	Cross validation			Prediction	
			N_c	*RMSECV*	R_{cv}	N_p	*RMSEP*
Tangxi-Dahongpao	SNV	6	70	0.361	0.537	30	0.382
Tangxi-Jiajiaozhong	MSC	5	70	0.137	0.609	30	0.194
Chun'an-Dahongpao	MSC	3	70	0.407	0.374	30	0.388
Chun'an-Jiajiaozhong	MSC	6	70	0.335	0.494	30	0.361

Abbreviations are number of samples in the calibration (N_c) and prediction (N_p) sets, number of factors (N_F) used, root mean square error of cross validation (*RMSECV*) and prediction (*RMSEP*), and correlation coefficient of cross validation (R_{cv})

CONCLUSION

From the results, it can be seen that there were relatively good correlations between measured SSC and predicted SCC by NIR spectra for the two varieties of loquats from two orchards; however, the results for acidity prediction were not as good as SSC. The results show that the modeling results were better for the data in full NIR spectral range (800~2500 nm) than that in short NIR (800~1100 nm) and long NIR (1100~2500 nm) spectra regions. We also found that derivative spectra were not as good as original spectra for modeling. The application of MSC or SNV correction processing can improve the results of acidity prediction. Models for SSC predictions yielded better results than those for acidity predictions, and the correlation coefficients between NIR spectra and SSC were much higher than those between NIR spectra and acidity.

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