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Application of NIR spectroscopy for firmness evaluation of peaches*

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Abstract: The use of near infrared (NIR) spectroscopy was proved to be a useful tool for quality analysis of fruits. A bifurcated fiber type NIR spectrometer, with a detection range of 800~2500 nm by InGaAs detector, was used to evaluate the firmness of peaches. Anisotropy of NIR spectra and firmness of peaches in relation to detecting positions of different parts (including three latitudes and three longitudes) were investigated. Both spectra absorbency and firmness of peach were influenced by longitudes (i, ii, iii) and latitudes (A, B, C). For modeling, two thirds of the samples were used as the calibration set and the remaining one third were used as the validation or prediction set. Partial least square regression (PLSR) models for different longitude and latitude spectra and for the whole fruit show that collecting several NIR spectra from different longitudes and latitudes of a fruit for NIR calibration modeling can improve the modeling performance. In addition, proper spectra pretreatments like scattering correction or derivative also can enhance the modeling performance. The best results obtained in this study were from the holistic model with multiplicative scattering correction (MSC) pretreatment, with correlation coefficient of cross-validation r_{cv}=0.864, root mean square error of cross-validation *RMSECV*=6.71 N, correlation coefficient of calibration r=0.948, root mean square error of calibration *RMSEC*=4.21 N and root mean square error of prediction *RMSEP*=5.42 N. The results of this study are useful for further research and application that when applying NIR spectroscopy for objectives with anisotropic differences, spectra and quality indices are necessarily measured from several parts of each object to improve the modeling performance.

Key words: Near infrared (NIR), Anisotropy, Peach, Firmness, Partial least square regression (PLSR)
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INTRODUCTION

Near infrared (NIR) spectroscopy technique has gained a great deal of attention in food quality analysis due mainly to its suitability for recording the spectra of solid and liquid samples at low cost without any pretreatment and in a nondestructive way (Sáiz-Abajo *et al*., 2004). The main characteristics hindering its expansion at first is that NIR spectra typically consist of broad, weak, non-specific, extensively overlapped bands (Blanco *et al*., 2000). Until multivariate calibration methods became widely available and accepted, NIR spectroscopy technique has been widely studied and applied. Partial least square regression (PLSR) developed by Wold and Martens in 1983 (Xu *et al*., 2007) is the most widely used method for NIR spectral modeling. The objective of PLS (partial least square) is to define a set of latent variables through the projection of the process and quality spaces onto new orthogonal subspaces by maximizing the covariance between the two spaces (Li *et al*., 2002). In NIR modeling process, the components of the matrix of spectral characteristics are extracted so as to maximize the covariance with the measured absorbance in the set of calibration samples. The relationships are developed from the training set and then applied to the set of unknowns (Hopke, 2003). PLS works nicely not only for analyzing the concentrations of specific chemicals but also for analyzing sample properties, such as color, hardness or viscosity, which produce a spectral response. NIR spectroscopy combined with PLSR method was proved to be a powerful tool for quality analysis of

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fruits such as mango, apple, pear, cherry, citrus, watermelon, etc. by many researchers (Clark *et al*., 2003; Liu *et al*., 2007; Lu R., 2001; McGlone *et al*., 2005; Schmilovitch *et al*., 2000; Subedi *et al*., 2007; Ying *et al*., 2005; Zou *et al*., 2007; Lu H.S. *et al*., 2006; Tian *et al*., 2007).

Fruits are anisotropic objects, appearing different physical and chemical properties or characteristics when measured in different directions. Wang (2004) studied the mechanical properties including failure stress, failure strain, failure energy and Young's modulus of pear tissue related to specimen orientation and location. His study showed that the mechanical properties were significantly affected by specimen orientation, latitude and depth, but not affected by the longitude of the specimen. Khan and Vincent (1993) did crack-opening tests (wedge penetration tests and notch tensile tests) on apple flesh. Their results showed that the tissue had marked anisotropy in its fracture properties. The flesh of the apple is split much more easily along the fruit's radius than, for example, in a direction parallel to the fruit's tangent. Also Khan and Vincent (2006) investigated the parenchyma of a range of apple varieties, either sectioned in a cryotome and observed under a light microscope, or freeze-dried and viewed under a scanning electron microscope. The morphology of the material varied according to the direction from which it was viewed. This anisotropy phenomenon increased from the outside to the inside of the cortex.

Fruit firmness, the ability of fruit flesh to resist compressive force, is one of the most important characteristics to estimate fruit maturity and quality. Generally, firmness is detected either by touch or by hand-held penetrometer measurement. Both these two measurements are destructive and the detected firmness can vary greatly with the skill and care taken by the operator. Recently, measurement of the optical properties of fruits has been one of the most successful nondestructive techniques for quality assessment. Optical techniques, NIR spectroscopy for instance, have received considerable attentions as a means for nondestructive evaluation of fruit firmness (van Dijk *et al*., 2006; Lu and Ariana, 2002; McGlone and Kawano, 1998; Park *et al*., 2003). However, the above studies of fruit firmness evaluation using NIR spectroscopy scarcely take fruit anisotropy into account. They mostly selected 1~4 points on the fruit for spectra acquisition and quality measurement. For example, McGlone and Kawano (1998) made two measurements on opposite sides of the fruit and averaged to give a mean penetrometer firmness for the fruit; Park *et al*.(2003) measured the firmness at four locations on each apple; Lu and Ariana (2002) and van Dijk *et al*.(2006) performed singular compression measurement on each fruit.

The objectives of this research were: (1) to investigate the anisotropy of the NIR spectra and firmness of white peaches related to different longitudes and latitudes; (2) to compare the performance of models using NIR spectra and firmness measured from different longitudes and latitudes of each fruit by PLSR method; (3) to investigate the usefulness of spectra pretreatments and nonlinear PLSR and weighted PLSR methods for improving modeling performance.

MATERIALS AND METHODS

Samples

A total of 180 white peaches were purchased from Jinhua County, Zhejiang Province and transported to the laboratory on June 30, 2006. Samples were stored at 25 °C and 60% relative humidity (RH) during the several days of experiment. Two thirds of the samples (120 peaches) were used for calibration models and the remaining one third (60 peaches) were used for prediction models. For each sample, spectra acquisition and firmness measurement were carried out in 2 h. The primary characters of the peaches were described in Table 1.

Table 1 Morphological properties of peach samples

	Max. dia. (mm)	Min. dia. (mm)	Height (mm)	Weight (g)
Max.	78.74	76.10	81.28	245.44
Min.	62.76	64.80	67.54	170.39
Average	73.89	70.10	73.66	203.92
SD	3.22	2.57	2.91	20.10

SD: Standard deviation

Experimentation

1. NIR spectra acquisition

NIR diffuse reflectance spectra were acquired using a Fourier transform (FT)-NIR spectrometer (Thermo Electron Corp., USA) equipped with an interferometer, an InGaAs detector, a bifurcated fiber-optic probe, and a quartz halogen light source (50 W). Software of OMINC 6.1a (Thermo Electron Corp., USA) was used for spectrometer setup and spectra acquiring operation. The parameters of spectrometer setup were as follows: resolution of 16 cm^{-1}, scan number of 64 times, mirror velocity of 0.9494 cm/s, and spectral range of 800~2500 nm. For each sample, nine spectra were collected corresponding to three longitudes (i, ii, iii) and three latitudes (A, B, C) as shown in Fig.1. The three longitudes were about 120° apart from each other. One of the three latitudes was at the equator and the other two were close to the stem end and the calyx end. Samples were placed directly upon the surface of the fiber probe by hand. Before peach spectra acquisition, a reference spectrum was collected from a whit Teflon block. The diffuse reflectance spectra of samples were saved as log(1/*R*), where *R* is the ratio of light intensity reflected from the sample to that reflected from the Teflon block.

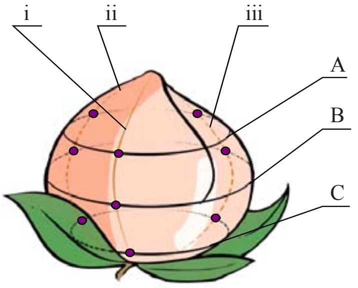

Fig.1 Nine testing positions corresponding to three longitudes (i, ii, iii) and three latitudes (A, B, C)

2. Firmness measurement

The firmness measurements were conducted using a standard 6-mm MT (Magness-Taylor) probe mounted in an Instron 5543 universal testing machine (Instron Corp., USA) with a loading rate of 20 mm/min, and interfaced to a computer to obtain continuous force-deformation curves. The firmness was measured at the corresponding locations where NIR diffuse reflectance spectra were acquired on each sample. Only maximum force (N) for penetration was used for the firmness test.

3. Data analysis

Nine diffuse reflectance spectra were collected: (iA), (iB), (iC), (iiA), (iiB), (iiC), (iiiA), (iiiB) and (iiiC). Analysis of variance (ANOVA) was applied to observe the anisotropic differences both of spectra and firmness. Spectra pretreatments and statistical modeling were carried out using software TQ Analyst (Thermo Electron Corp., USA). Spectra pretreatments include scattering correction and derivative. PLSR method was used to establish the chemometrics models. The calibration models include two validation procedures: cross-validation and external validation. Cross-validation was performed on the calibration samples based on excluding one observation from the calibration model, which is leave-one-out cross-validation. Since the validation samples in cross-validation procedure are from the calibration sample set, a comparable kind of spectral variability can be expected. External validation was performed on the prediction sample set. In this way, the ability of the calibration model to withstand unknown variability is assessed. Beside linear PLSR, other two PLSR methods (nonlinear PLSR and weighted PLSR) were also to see whether the modeling performance could be improved. The accuracy of the models was defined as correlation coefficient of calbration and cross-validation (r and r_{cv}), root mean square errors of calibration, cross-validation and prediction (*RMSEC*, *RMSECV* and *RMSEP*).

RESULTS AND DISCUSSION

Spectra anisotropic differences

NIR diffuse reflectance spectra were recorded at 1102 points in the region of 800~2500 nm. Fig.2 shows the average spectrum of all the samples and the standard deviation (variance) of spectral data at 1102 points. The standard deviation obviously decreased above 1400 nm and revealed two vales around 1450

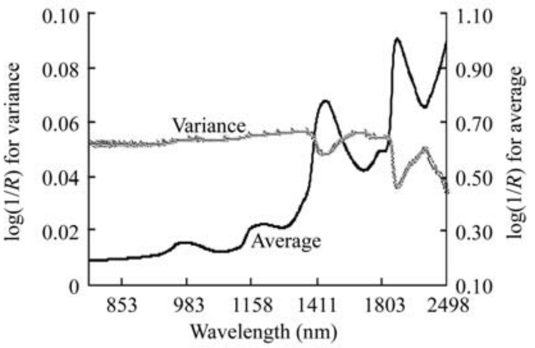

Fig.2 Average spectrum of all samples and the standard deviation (variance) of spectral data at 1102 points in the region of 800~2500 nm

nm and 1940 nm corresponding to the two peaks on average spectrum, which are related to O-H first overtones and O-H stretching vibration and deformation vibration of water.

In order to investigate spectra anisotropic difference of peaches, ANOVA was applied to each sample by calculating the *F* values of three average spectra in the full wavelength range related to longitude or latitude. To take longitude (i, ii, iii) for example, the three spectra at each longitude were averaged, and the *F* value of the absorbance of three average spectra (S-i, S-ii, S-iii) were calculated by ANOVA method. The result revealed an *F* value and an *F* critical value (α=0.05). By comparing the two values, it can be clearly found out whether the absorbance of the spectra at different longitudes changed obviously or not. The same procedure was applied to three latitudes (A, B, C). Each sample has two *F* values corresponding to longitude and latitude, respectively. Because *F* critical value is only related to the freedom degrees (*df*) of the dataset for ANOVA procedure, this value was the same for all the samples. Fig.3 shows the *F* values of longitude and latitude variance analyses of spectra in the full wavelength range for each sample. According to *F*-verification principle, the absorbance of the samples above the *F* critical line (more than two thirds) changed obviously with longitude or latitude variance, while the samples below the *F* critical line did not. Therefore, it is hard to conclude that longitude or latitude will influence the spectral absorbance.

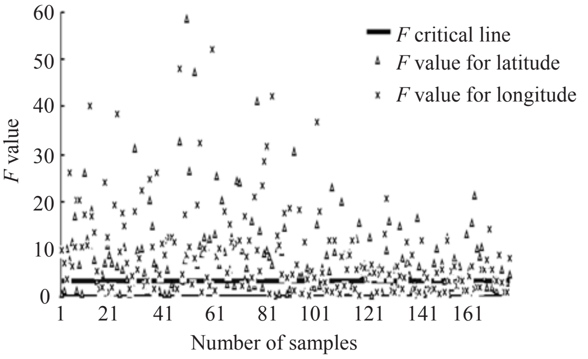

Fig.3 *F* values of longitude and latitude variance analyses of spectra in the full wavelength range for each sample

Another way was tried to investigate this problem. To take longitude (i) for example, the average absorbance of the averaged spectrum at longitude (i) of each sample was calculated firstly, and 180 average absorbance values were obtained. Applying the same procedure to the other two longitudes (ii, iii), a matrix (3×180) can be obtained, 3 representing three longitudes and 180 representing the number of samples. Also using ANOVA method, the *F* value can be obtained to determine whether the average absorbency changed obviously with longitudes or not. The same procedure was used to observe the spectral changes with latitudes. Table 2 shows the ANOVA results of average absorbency of different longitudes and latitudes. Both for longitude and latitude, $F_{0.05}<F<F_{0.01}$, concluding that the average absorbency changed obviously with longitude and latitude at level 0.05 but not at level 0.01.

Firmness anisotropic differences

Corresponding to the spectra collecting positions of each sample, nine firmness measurements were carried out. Firmness anisotropic differences were also analyzed by ANOVA method. The ANOVA results (*F* values) for each longitude and latitude factor were shown in Fig.4. All *F* values were greater than *F* critical value at level 0.01, which indicated that firmness of peaches was influenced by longitude and latitude. And latitude effect was more evident than longitude effect.

Table 2 ANOVA of average absorbency of different longitudes and latitudes

Source		*SS*	*df*	*MS*	*F* value	*F* critical value	
						$F_{0.05}$	$F_{0.01}$
Longitude	Factor	0.027863	2	0.013931	4.599812	3.012507	4.64489
	Error	1.626393	537	0.003029			
	Total	1.654256	539				
Latitude	Factor	0.024709	2	0.012354	4.528424	3.012507	4.64489
	Error	1.465041	537	0.002728			
	Total	1.489750	539				

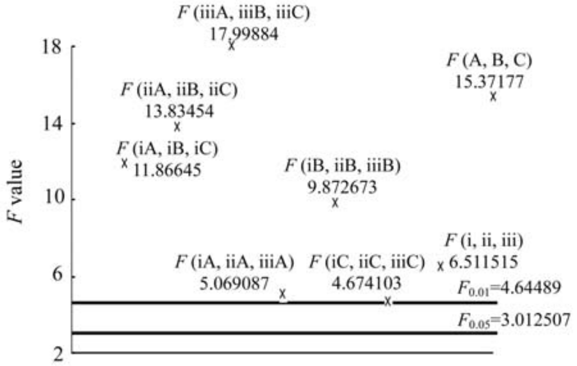

Fig.4 ANOVA results of peach firmness measurements according to different longitude and latitude

NIR modeling

1. Influence of anisotropic differences

From the results of the above section, it is necessary to observe the influence of anisotropic differences on NIR modeling results, for both absorbance of NIR spectra and firmness are changed in different degrees along with longitudes and latitudes. Seven calibration models were established using PLSR method. For each sample, three spectra at each longitude were averaged. For a certain longitude or latitude model, the average spectra of all 180 samples corresponding to this longitude or latitude were used. In addition, a holistic model was established using the mean spectrum of nine spectra (corresponding to three longitudes and three latitudes) of each sample. Table 3 shows the results of these models, including r, r_{cv}, *RMSEC*, *RMSECV* and *RMSEP*. The results of the holistic model were better than those of other models for a certain longitude or latitude, with relatively high r and r_{cv}. The small differences between *RMSEC*, *RMSEP* and *RMSECV* indicate that the model was robust not only for the observations in the calibration dataset but also for external samples.

2. Improvement of the holistic model

The models established were based on original spectra using linear PLSR method. In order to improve the modeling performance, spectra pretreatments including scattering correction and derivative and the other two PLSR methods (nonlinear PLSR and weighted PLSR) were applied to the holistic model. Multiplicative scattering correction (MSC) or the first derivative treatments can improve the modeling performance, with r increasing to 0.909 or 0.948. When both MSC and the first derivative treatments were applied, r increasing to 0.981, but the difference between *RMSEC* and *RMSEP* also increasing (*RMSEC*=4.21 N, *RMSEP*=7.48 N). Nonlinear PLSR method educed the same results as linear PLSR method did, while weighted PLSR method educed worse results. Fig.5 shows the PLSR modeling results with MSC pretreatment of the holistic model. The *RMSEP* of this model was 5.42 N.

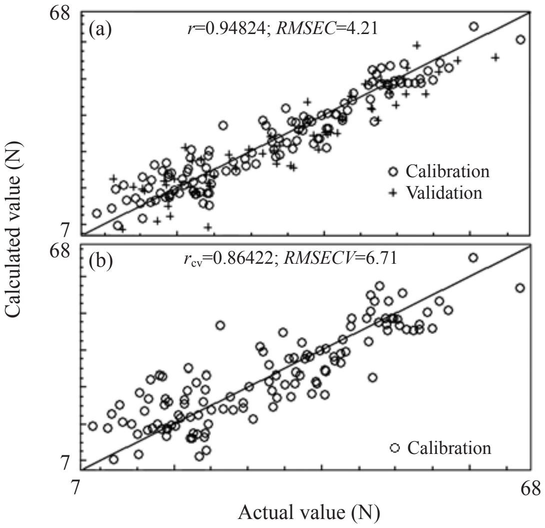

Fig.5 PLSR modeling results with MSC pretreatment of the holistic model. (a) Calibration result; (b) Cross-validation result

Table 3 PLSR modeling results for different longitudes and latitudes

		Factors	r_{cv}	*RMSECV* (N)	r	*RMSEC* (N)	*RMSEP* (N)
Longitude	i	5	0.810	8.20	0.834	7.70	7.82
	ii	2	0.867	6.23	0.875	6.06	7.18
	iii	5	0.800	8.51	0.829	7.93	7.49
Latitude	A	6	0.780	8.89	0.846	7.52	7.11
	B	5	0.871	6.78	0.889	6.34	7.04
	C	5	0.823	7.16	0.846	6.72	7.61
Holistic model		6	0.871	6.52	0.894	5.94	5.96

CONCLUSION

This study indicates the anisotropic differences of NIR spectra and firmness of white peach fruit. NIR spectroscopy together with PLSR method has been proved to be a valid tool for peach firmness prediction. PLSR results of models for different longitudes and latitudes spectra and the holistic model show that collecting several NIR spectra from different longitudes and latitudes of a fruit for NIR calibration modeling can improve the modeling performance. In addition, proper spectra pretreatments like scattering correction and derivative also can enhance the modeling performance. The best results obtained in this study were from the holistic model with MSC pretreatment, with r_{cv}=0.864, $RMSECV$=6.71 N, r=0.948, $RMSEC$=4.21 N and $RMSEP$=5.42 N. The results of this study are useful for further research and application that when applying NIR spectroscopy for objectives with anisotropic differences, spectra and quality indices are necessarily measured from several parts of each object to improve the modeling performance.

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