

Measurement of Soluble Solids Contents and pH in Orange Juice Using Chemometrics and Vis–NIRS

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The potential of visible and near-infrared reflectance spectroscopy (vis–NIRS) was investigated for its ability to nondestructively detect soluble solids contents (SSC) and pH in orange juices. A total of 104 orange juice samples were used for vis–NIRS at 325–1075 nm using a field spectroradiometer. Wavelet packet transform, standard normal variate transformation (SNV), and Savitzky–Golay first-derivative transformation were applied for the preprocessing of spectral data. The chemometrics of partial least-squares (PLS) regression analysis was performed on the processed spectral data. The evaluation of SSC and pH in orange juices by PLS regression with SNV showed the highest accuracy of the three preprocessing methods. The correlation coefficient (r), standard error of prediction, and the root-mean-square error of prediction for SSC were 0.98, 0.68, and 0.73, respectively, whereas those values for pH were 0.96, 0.06, and 0.06, respectively. The “fingerprint” representing features of orange juices or reflecting sensitivity to some elements at a certain band was proposed on the basis of regression coefficients. It is very useful in the field of food chemistry and further research on other materials. It is concluded that the vis–NIRS technique combined with chemometrics is promising for the fast and nondestructive detection of chemical components in orange juices or other materials.

KEYWORDS: Orange juice; vis–NIR; SSC; pH; preprocessing; PLS

INTRODUCTION

With the development of the food industry, the problems of food additives and safety have attracted much attention, especially for beverages. Orange juice is considered to be one of the most important and common beverages in people’s daily life. Its quality is defined by physical characteristics (fluid, color, and odor) and chemical parameters [soluble solids content (SSC), pH, carbohydrates, and vitamins], which determine the taste and nutrition of orange juices.

SSC and pH are two significant properties in orange juices that affect the consumer’s appreciation for the selection of beverages. The SSC (I) in the fruit juice is mainly sugars, such as fructose, sucrose, and glucose, and pure fruit juice contains ~9–15% of SSC. In orange juice, acids are also important sources of nutrition and freshness with different kinds of organic acids, including citric, tartaric, and malic acids (2). Because organic acids have different abilities to dissociate hydrogen ion, the pH calculated by $-\log [H^+]$ was used to show the acidity in orange juice. Also, the pH plays an important role in the food processing industry related to the variation of color, microbial control, taste, and authentication of food. Because a great deal of nutrient elements will be lost in the processing of fresh orange juices, sugars, acids, water, and other additives will be added into the juice to adjust the taste and color, which is where the problem of adulteration of beverages consequently

appears. All of these factors have emphasized the need for reliable techniques to authenticate orange juices.

There are many methods to determine the internal quality of orange juices reported in the literature. Common detecting techniques used in the field of food chemistry are fluorescence analysis, chromatographic determination, photospectrometric analysis, electroanalysis, and capillary electrophoresis (3, 4). Hu et al. (5) used the fluorescence technique to detect adulteration of citrus juice with the emission wavelength region changing between 284.6 and 296.5 nm. A chemiluminescence method for the determination of citric acid using tris(2,2′-bipyridine) ruthenium was also developed by some researchers (6). Saavedra et al. (2) developed and validated a capillary electrophoresis method for the direct measurement of organic acids in fruit juice. Scordino and his partners (7) applied high-performance liquid chromatography (HPLC), ultraviolet (UV), and mass spectra to test and analyze the quality of orange juices. Most of these methods are based on the complex processing for samples, and the use of chemical reagents is also a problem if the economic benefit and safety are considered in the experiment. All of these methods are categorized as destructive, and they are not very simple or convenient in practical application. For some traditional testing methods, it takes a long time to obtain the testing result for one sample from preparation to the end (8). Thus, a rapid, safe, and nondestructive method is needed to qualify for testing the internal quality of orange juices.

Recently, research has been focused on the development of a vis–NIRS technique for its potential application in the field

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Table 1. Brands of Orange Juice in Experiment

brand	class	production company	SSC		pH	
			range	mean	range	mean
Minute Maid	beverage	Coca-Cola	2.5–11.75	5.42	3.46–3.75	3.60
Masterkong Day C	beverage	Masterkong	2.00–11.50	5.45	3.30–3.53	3.41
Qoo	beverage	Coca-Cola	2.75–13.75	6.36	3.54–3.76	3.66
Nongfu Orchard	pure	Nongfuspring	2.50–12.00	5.60	3.95–4.08	4.02
Masterkong	beverage	Masterkong	2.00–12.25	5.57	3.37–3.57	3.47
Unif	beverage	Unif	2.00–11.00	4.90	3.56–3.71	3.63
Great Lakes	pure	Great Lakes	2.00–13.00	6.36	3.91–4.29	4.00
Huiyuan	pure	Huiyuan	3.25–12.00	7.79	3.90–4.02	3.94

of food chemistry. The advantage of vis–NIRS is that not only can chemical structures be assessed through the analysis of the molecular bonds in the visible and near-infrared reflectance spectrum but also a characteristic spectrum that represents the “fingerprint” of the sample can be built (9). He et al. (10) analyzed apple brands using NIRS with principal component analysis (PCA) and a BP neural network (BPNN) model. Tsuchikawa and Hamada (11) proposed time-of-flight near-infrared spectroscopy to detect sugar and acid contents in apples, and three chemometric models were built, including partial least-squares regression (PLSR), principal component regression (PCR), and multiple linear regression (MLR). In other papers, nondestructive determination of solids and carotenoids in tomato products by near-infrared spectroscopy was also presented (12). Meanwhile, classification and adulteration of beverages were studied by some researchers with NIRS (13). Nevertheless, SSC and pH in orange juices were little calibrated using vis–NIRS. Due to the hidden information in spectral data, at present, particular attention has been paid to the data mining of numerous spectral data with chemometrics. PLSR has been proved to be a more excellent method than the others, such as MLR and PCR (11, 14, 15). In the analysis of spectra, there are large baseline shifts and noises in the spectra with a broad wavelength region. Thus, the selection of suitable preprocessing methods is also an important step in the process of spectral analysis. Dou et al. used four different preprocessing methods [first derivative, second derivative, standard normal variate transformation (SNV), and multiplicative scatter correction (MSC)] to process NIR spectra of compound aminopyrine phenacetin tablets, and the SNV preprocessing spectra were found to provide the best results (16). Also, some researchers applied wavelet packet transform (WPT) in pattern recognition of NIRS data (17).

The objective of this study was to assess the potential of vis–NIRS as a rapid and nondestructive technique to detect SSC and pH in orange juices depending on the multivariate calibration PLS with different preprocessing methods [WPT, SNV, and Savitzky–Golay first-derivative (S. Golay first-der)]. “Fingerprint” analysis based on regression coefficients was also proposed so that further research on other materials would be more feasible.

MATERIALS AND METHODS

Sample Preparation and Reference Method. Eight brands of orange juices purchased from the local market were selected for the vis–NIRS analysis (shown in Table 1), and each brand includes a certain number of samples produced at different dates. For analytical purposes, the samples were also diluted. Finally, 104 samples were obtained in this experiment. They were placed in airtight glass bottles, stored in an ice-filled cooler, and transported to the laboratory, where they were kept at cold temperature (4 ± 1 °C). All orange juice samples were first allowed to equilibrate to room temperature (25 °C) before vis–NIRS analysis.

The reference methods for determination of SSC and pH were chosen by considering the precision and convenience of measurement. Samples were taken for SSC measurement by using an Abbe benchtop refractometer (2WAJ 0–95 °Brix, Shanghai, China), with a 0.02 °Brix accuracy using temperature correction. A pH-meter (SJ-4A, Instrument Co. Ltd., Shanghai, China) with an accuracy of 0.01 was used to measure the pH.

Reflectance Measurement. Orange juice samples were poured about half full into glass sample containers of 120 mm diameter and 10 mm height. All samples were prepared for vis–NIRS analysis at 325–1075 nm. For each sample, three reflecting spectra were taken for three equidistant rotation positions of $\sim 120^\circ$ around the container center with a field spectroradiometer [FieldSpec HandHeld (HH), VNIR (325–1075 nm)], Analytical Spectral Devices (ASD), Inc., Boulder, CO], using RS² V4.02 software for Windows designed with a graphical user interface (GUI) from ASD. The instrument uses a sensitivity 512-element, photodiode array spectroradiometer, with the resolution of 3.5 nm. The scan number for each spectrum was set to 10 at the same position; thus, a total of 30 individual spectra were properly stored for later analysis. Considering its 25° field-of-view (FOV), the spectroradiometer was placed at a height of ~ 100 mm and 45° angle away from the center of the sample container. A light source of Lowell prolam 14.5 V bulb/128690 tungsten halogen was placed ~ 300 mm away from the viewing area. To achieve the relative reflectance measurements, the white reference (a white panel purchased with the spectroradiometer used as white reference) was collected before scanning samples to obtain a nice, clean, 100% reference line.

Preprocessing of Spectral Data. Due to the potential system imperfection, obvious scattering noises could be observed at the beginning and end of the spectral data. Thus, the first and last 75 wavelength data were eliminated to improve the measurement accuracy, that is, all visible and NIR spectroscopy analysis was based on 400–1000 nm. The above spectral data preprocessing was finished in ViewSpec Pro V4.02 (Analytical Spectral Devices, Inc.). Absorbance for the scan was recorded as $\log [1/R]$, and all spectral records were checked visually and averaged. The absorbance wavebands were then preprocessed using WPT, SNV, and S. Golay first-der, respectively.

Wavelet transform (WT) is a very popular kind of operation today due to its application in chemometrics and signal processing (18, 19), whereas WPT (20) is a derivative of WT that has many advantages in the extraction of information from the certain time and frequency. In this experiment, WPT was proposed as a preprocessing method for denoising. The wavelet function *symlets 6* was adopted to decompose the wavelet packet into five layers, *wpbmpen* was used to determine the threshold, and noises in the spectra were eliminated via the function *wpdencmp* (21). WPT was performed in software MATLAB 7.01 with the edited program.

SNV removes the multiplicative interferences of scatter, particle size, and the change of path length (22). For an individual spectrum to be processed by SNV, it is calculated as

$$x_{i,\text{SNV}} = (x_{i,k} - \bar{x}_i) / \sqrt{\frac{\sum_{k=1}^m (x_{i,k} - \bar{x}_i)^2}{(m-1)}} \quad (1)$$

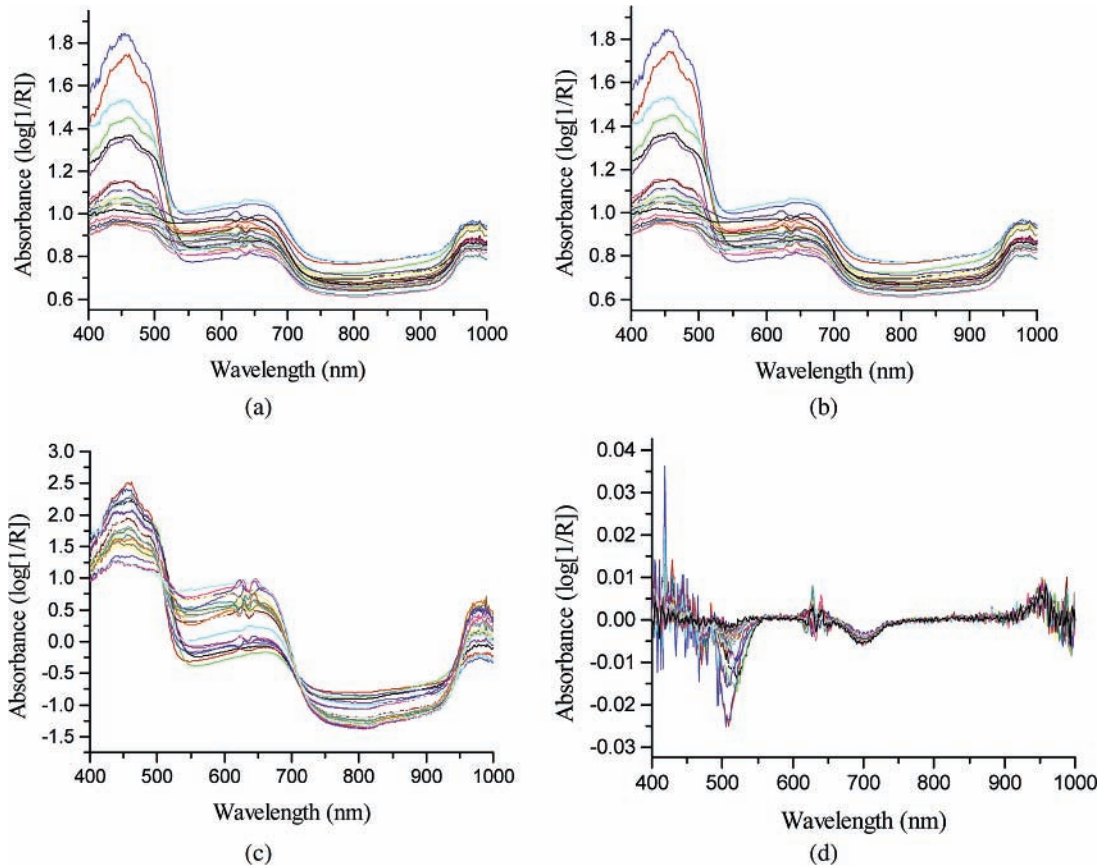


Figure 1. (a) Original absorbance spectra of orange juices; spectra processed by (b) WPT, (c) SNV, and (d) S. Golay first-der.

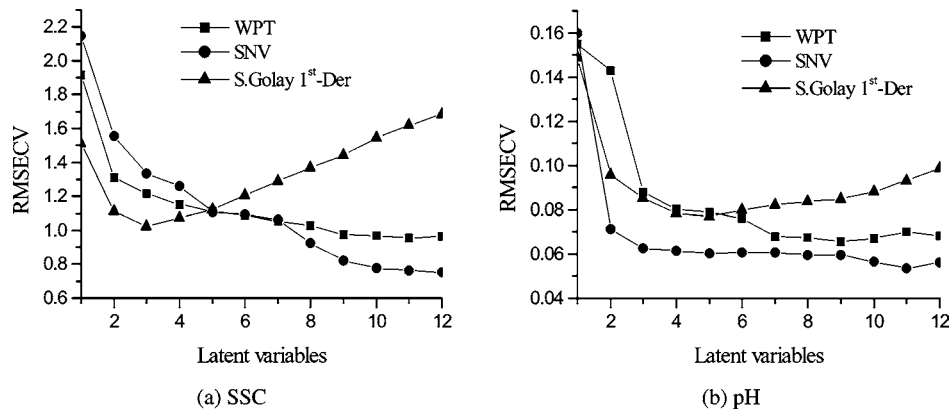


Figure 2. Calibration curves for WPT, SNV, and S. Golay first-der in models for SSC (a) and pH (b).

where $x_{i,SNV}$ is the transformed element, $x_{i,k}$ is the original element, \bar{x}_i is the mean of spectrum i , $k = 1, 2, \dots, m$, m is the number of variables in the spectra, $i = 1, 2, \dots, n$, and n is the number of the validation set.

Another preprocessing method first derivative is used to remove background and increase spectral resolution. Savitzky–Golay (23), which is a moving window averaging method, is used as a smoothing method in the first derivative, and the number of smoothing is three. It is very crucial to select the proper differentiation width (24). Generally, the width should not exceed 1.5 times the half-width of the absorbance peak in the spectra.

Partial Least-Squares Regression Analysis. Partial least-squares (PLS) regression with full cross-validation was conducted on the spectra at 400–1000 nm to analyze the SSC and pH of orange juices. PLS is a bilinear modeling method in which the original independent information (\mathbf{X} variable) is projected onto a small number of latent variables (LVs) to simplify the relationship between \mathbf{X} and \mathbf{Y} for predicting with the smallest number of LVs (25). The \mathbf{Y} variable is actively used in assessing the LVs to ensure that the first one is most relevant for predicting the \mathbf{Y} variable.

The first step in PLS is to decompose the matrix, and the model is

$$\mathbf{X} = \mathbf{TP} + \mathbf{E} \quad (2)$$

$$\mathbf{Y} = \mathbf{UQ} + \mathbf{F} \quad (3)$$

In these equations, \mathbf{T} and \mathbf{U} are the score matrices of the \mathbf{X} matrix and the \mathbf{Y} matrix, \mathbf{P} and \mathbf{Q} are the loading matrices of the \mathbf{X} matrix and the \mathbf{Y} matrix, and \mathbf{E} and \mathbf{F} are the errors that come from the process of PLS regression.

The second step is that \mathbf{T} and \mathbf{U} are processed by linear regression. It must build the linear correlation

$$\mathbf{U} = \mathbf{BT} + \mathbf{E} \quad (4)$$

where \mathbf{B} is the matrix of diagonally regressed coefficients. To reach this object, the coordinate of \mathbf{T} is rotated.

The cross-validation was performed on the calibration samples based on excluding a certain number of observations for the calibration model and used to determine the optimal number of PLS LVs. Due to

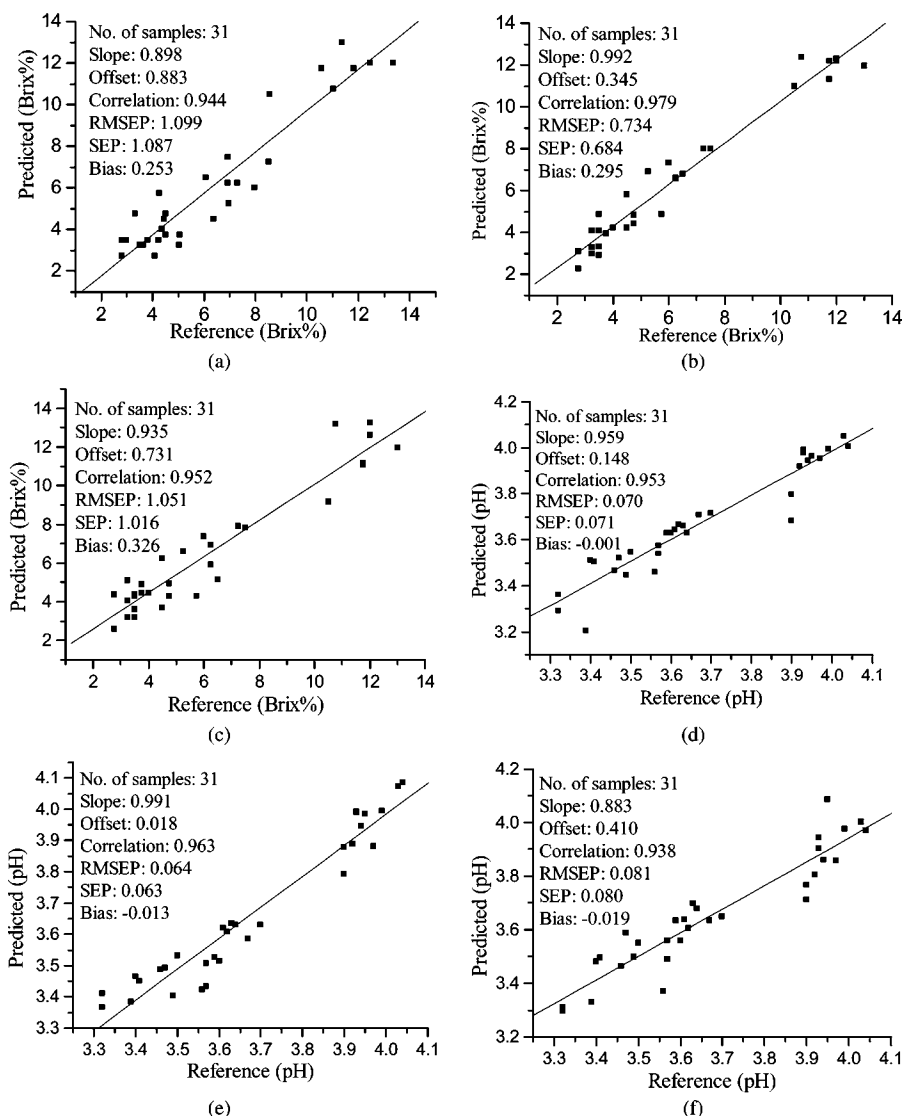


Figure 3. Reference versus predicted values for (a–c) SSC and (d–f) pH by WPT, SNV, and S. Golay first-der.

overlapping of the overtones from the different groups, the PLS method was applied to convert the complex spectral data into analytical parameters. Thus, the number of significant PLS LVs was chosen by using the predicted residual error sum of squares (PRESS) value for every possible LV based on cross-validation (26, 27). The PRESS value was the sum of the squared difference between the predicted and the known concentrations.

SNV, S. Golay first-der, and the whole calibration and validation process were achieved in The Unscrambler 9.5 (CAMO Process AS), a statistical software for multivariate data analysis and experimental design.

RESULTS AND DISCUSSION

Features of Visible and NIR Spectra. Figure 1a shows the 25 original spectra for 25 samples selected randomly from orange juice samples. Considerable noise appeared in the wavelength region at 400–500 and 950–1000 nm, and it could be eliminated by different preprocessing methods. The shape of the spectra was quite homogeneous, and no outliers were identified by the naked eye. Some peaks and valleys representing the characteristics of orange juices including hidden information of different elements and their quantities were obviously shown in the spectra.

There are consistent baseline shifts and bias in the spectra due to the light scattering or concentration variation of samples.

Table 2. Calibration and Cross-Validation Results for SSC and pH in Orange Juices from the Visible and NIR Spectra^a

	SSC (Brix %)				pH	
	2.00–13.75				3.30–4.29	
range	2.00–13.75				3.30–4.29	
mean	5.77				3.69	
model	1	2	3	4	5	6
LVs	4	9	3	7	3	4
calibration						
slope	0.92	0.98	0.94	0.93	0.93	0.93
offset	0.40	0.13	0.29	0.25	0.26	0.26
correlation	0.96	0.99	0.97	0.97	0.96	0.96
SEC	0.97	0.55	0.84	0.06	0.06	0.06
RMSEC	0.97	0.54	0.83	0.06	0.06	0.06
bias (10^{-7})	2.2	2.03	2.41	-0.36	-0.82	-1.05
cross-validation						
slope	0.93	0.96	0.94	0.93	0.92	0.93
offset	0.41	0.19	0.36	0.25	0.28	0.26
correlation	0.95	0.97	0.96	0.95	0.96	0.93
SEC	1.16	0.83	1.03	0.07	0.06	0.08
RMSECV	1.15	0.82	1.03	0.07	0.06	0.08
bias	0.02	-0.01	0.01	-0.0008	-0.0001	-0.0018

^a Models: WPT- 1 and -4, SNV-2 and -5, S. Golay first-der-3 and -6.

The light does not always travel the same distance in the sample before it is detected. A longer light traveling path corresponds to a lower relative reflectance value, because more light is absorbed. This causes a parallel shift of the spectra. This kind

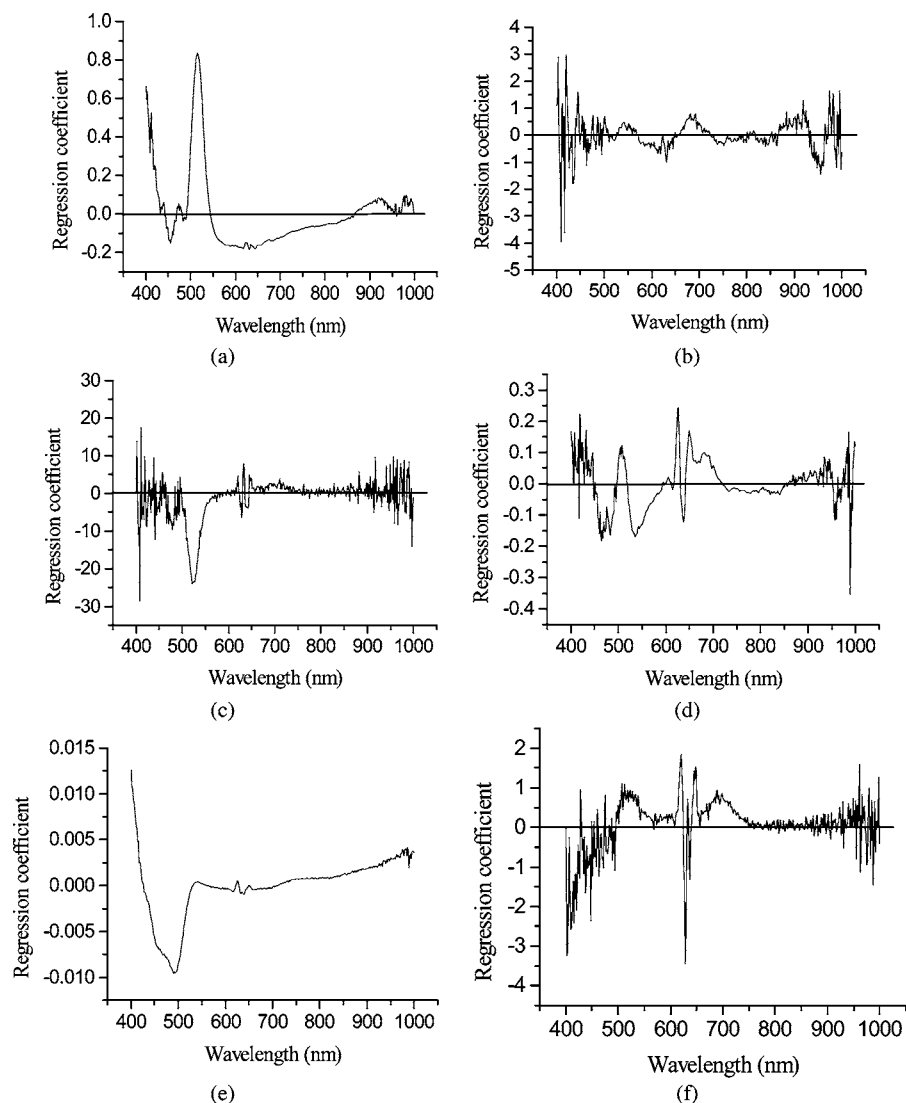


Figure 4. Regression coefficients obtained after optimal number of LVs in PLS models. The number of PLS LVs (a–c) was 4, 9, and 3 for SSC and (d–f) 7, 3, and 4 for pH preprocessed by WPT, SNV, and S. Golay first-der, respectively.

of variation is not useful for the calibration models and needs to be eliminated by data preprocessing techniques.

Panels **b**, **c**, and **d** of **Figure 1** show the spectra of orange juices processed by WPT, SNV, and S. Golay first-der. It is quite obvious that the peak and valley positions of the processed spectra are corresponding to the valleys or peaks in the original spectra (**Figure 1a**). It can be seen that denoising of WPT did not eliminate any important feature of the spectra, and then all of the relevant chemical information was retained for modeling. The SNV method eliminated the baseline shifts of the spectra (22) and made the peaks and valleys more obvious, such as the wavelength range of 600–700 nm. S. Golay first-der caused great changes in the slopes of the raw spectra, and many overlapped peaks could be differentiated.

The main constituents in orange juices are organic acids (citric, tartaric, malic acid, etc.), sugars (fructose, sucrose, etc.), vitamins, and some natural pigments (flavonoids and carotenoids). In the visible region, pigments would produce some influences on the variation of absorbance in the spectra. However, the relationship between pH and some pigments can provide information to build PLS calibration about the variation of pH value in the visible region. Also, the chemical structure of sugars and some organic acids was related with the NIR region.

Multivariate Calibration. The calibration models for SSC and pH with preprocessed spectra were developed using PLS regression with cross-validation. One hundred and four samples were split into two groups. Seventy-three samples were used for the calibration, and the residual 31 were used for the validation. It is eligible to build and evaluate the models. To evaluate the results, standard error of calibration (SEC) and correlation coefficient (r_c) and standard error of cross-validation (SECV) and correlation coefficient (r_{cv}) were considered.

Good models should have lower SEC and SECV and higher correlation coefficients (r) but smaller differences between SEC and SECV, because large ones indicate that too many LVs are introduced in the model and the noises are also modeled. In addition, the root-mean-square error of cross-validation (RMSECV) was used to determine the optimal model without “overfittedness” or “underfittedness” (27).

In **Figure 2**, the RMSECV curves for the mean-centered, WPT-, SNV-, and S. Golay first-der-corrected samples display small values (close to 0) with as few LVs as possible at 4, 9, and 3 LVs for SSC and 7, 3, and 4 LVs for pH, respectively. The corresponding vectors were then used for the secondary samples that had been corrected and mean-centered on the basis of the mean vector for the corrected samples. From **Figure 2**, RMSECV does not appear to change significantly after the

certain number of LVs, which were used as PLS LVs, simplifying calibration models.

Reasonable models were obtained by PLS multivariate calibration with full cross-validation, and the results are shown in **Table 2**. This calibration revealed that some differences existed among different models with different preprocessing methods. The models for SSC and pH using SNV yield the best results in the cross-validation. Whether for SSC or pH, the SECV, RMSECV, and bias are lowest, and correlation coefficients are highest in models built by SNV-processed spectra. It is interesting to note that the number of LVs selected by PLS regression models varied. This effect is probably due to the differences in the signal-to-noise ratio on preprocessing procedures.

Prediction Results of PLS Regression Analysis for SSC and pH. On the basis of the above, three PLS models were applied to predict 31 residual samples after similar mathematical preprocessing to the calibration ones. The prediction results of SSC and pH in orange juices using three different preprocessing methods are shown in **Figure 3**. The regression line represented ideal results, and so the closer the points are to this, the better was the model. The high correlation coefficients (r) and low standard error of prediction (SEP) and the root-mean-square error of prediction (RMSEP) indicated that these models built by PLS with WPT, SNV, and S. Golay first-der could qualify for predicting SSC and pH of orange juices.

All of the models developed had r in prediction >0.93 , and the r of 0.98 and 0.96 in PLS with the SNV model for SSC and pH is the highest. SEP and RMSEP were also calculated, showing the evaluating standard for the quality of models and the predictive abilities. In the case of PLS regression analysis with WPT and S. Golay first-der, the SEP values between measured and predicted SSC were 1.09 and 1.02, respectively (see **Figure 3b**). However, in the case of SNV preprocessing, the SEP was improved to 0.68, which is much lower than that in the two others, as well as RMSEP. Interestingly, the application of the SNV preprocessing method for pH prediction was also the best in multivariate statistical analysis. The 0.06 SEP and 0.06 RMSEP were the lowest (see **Figure 3e**). In view of these prediction results, it is very important to select a prior preprocessing method for the analysis of spectral data. In addition, it is possible to find a good calibration equation concerned with SSC and pH in orange juice based on the vis-NIRS technique with proper chemometrics by employing a much more explanatory variable.

Fingerprint Analysis Based on Regression Coefficients. With different preprocessing techniques, the fingerprints reflecting the characteristics of spectra for SSC and pH were obtained on the basis of regression coefficients (**Figure 4**). It could be seen that the shape and trend of fingerprints were similar for SSC or pH, respectively, although different signal correction methods were used before calibration models were built. From **Figure 4a–c**, it was found that wavelengths of 410, 520, 640, 930, and 990 nm might be of particular importance for the SSC calibration. Furthermore, the regression coefficients shown in the figures calculated from different numbers of LVs give significant weights at the wavelength regions referred to above. The regression coefficients shown in **Figure 4d–f** also have strong peaks and valleys at certain wavelengths, such as 410, 490, 520, 620, 640, and 990 nm, related to pH.

In the visible region, the pigments in orange juice have some influences, and changes in the pH of the juice could produce shifts in the absorbance of particular wavelengths in the visible region related with those pigments (28). Thus, the variation of

absorbance and the appearance of some peaks such as wavelength at 520 and 620 nm may be affected by carotenoids and flavonoids in orange juices. However, when models are built, the whole wavelength is used in PLS analysis, which considered the concentration matrix (Y variable). Thus, SSC and pH were also related to these peaks in the visible region. The band at 930 nm possibly resulted from C–H stretch third overtone from sugars, and spectral variation at 990 nm was produced by the O–H stretch second overtone from sugars, organic acids, and flavonoids (29). The attempt to find a fingerprint for SSC and pH can be valuable due to the lack of this information in visible and NIR spectroscopy of orange juice or other materials.

It is concluded that PLS regression as chemometrics combined with the vis-NIRS technique for evaluation of chemical compositions in orange juices is successfully applied by simple models and feature extraction techniques. The statistic parameters of calibration and validation showed that the PLS regression model was an available alternative for quality detection of orange juices based on vis-NIRS. Multiplicative signal correction was proposed and used as an effective preprocessing method in that the calibration models for the internal quality of orange juices were optimized. It is also necessary to select an optimal preprocessing method to improve the accuracy and reliability of regression models. On the basis of PLS regression coefficients, the fingerprint representing features of orange juice or reflecting sensitivity to some elements at a certain band was proposed. The fingerprint analysis is very useful in the field of food chemistry, and further research on other materials is needed to improve the reliability and precision of this technology.

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