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A comparative study for the quantitative determination of soluble solids content, pH and firmness of pears by Vis/NIR spectroscopy

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ABSTRACT

Visible and near infrared (Vis/NIR) spectroscopy was investigated to determine the soluble solids content (SSC), pH and firmness of different varieties of pears. Two-hundred forty samples (80 for each variety) were selected as sample set. Two-hundred ten pear samples (70 for each variety) were selected randomly for the calibration set, and the remaining 30 samples (10 for each variety) for the validation set. Partial least squares (PLS) and least squares-support vector machine (LS-SVM) with different spectral preprocessing techniques were implemented for calibration models. Different wavelength regions including Vis, NIR and Vis/NIR were compared. It indicated that Vis/NIR (400–1800 nm) was optimal for PLS and LS-SVM models. Then, LS-SVM models were developed with a grid search technique and RBF kernel function. All LS-SVM models outperformed PLS models. Next, effective wavelengths (EWs) were selected according to regression coefficients. The EW-LS-SVM models were developed and a good prediction precision and stability was achieved compared with PLS and LV-LS-SVM models. The correlation coefficient of prediction (r_p), root mean square error of prediction (RMSEP) and bias for the best prediction by EW-LS-SVM were 0.9164, 0.2506 and −0.0476 for SSC, 0.8809, 0.0579 and −0.0025 for pH, whereas 0.8912, 0.6247 and −0.2713 for firmness, respectively. The overall results indicated that the regression coefficient was an effective way for the selection of effective wavelengths. LS-SVM was superior to the conventional linear PLS method in predicting SSC, pH and firmness in pears. Therefore, non-linear models may be a better alternative to monitor internal quality of fruits. And the EW-LS-SVM could be very helpful for development of portable instrument or real-time monitoring of the quality of pears.

1. Introduction

Fruits are sorted manually or automatically on the basis of size, color, shape and surface defects. However, other parameters which could better meet consumer expectations like soluble solids content (SSC), pH, firmness, etc. are traditionally determined with destructive techniques on a fruit sample. Therefore, it is essential to develop efficient and non-destructive methods for measuring the internal attributes of fruit. Vis/NIR or NIR spectroscopy is a fast, easy-to-use and non-destructive analytical technique (Day and Fearn, 1982; Huang et al., 2008). One of the main advantages of this technology 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. NIR spectroscopy was sensitive to the concentrations of organic materials, which involved the response of molecular bonds C—H, O—H and N—H. SSC, pH and firmness can be reflected by these organic molecules. Therefore, compared with Vis/NIR spectroscopy, single NIR spectroscopy has been more widely employed to assess the internal quality of fruits such as apple (Liu et al., 2007a,b), plum (Louw and Theron, 2010), orange (Shao et al., 2009), banana (Liew and Lau, 2012), olive (Morales-Sillero et al., 2011), apricot fruit (Bureau et al., 2009), and peach (Carlomagno et al., 2004).

Parameters such as pH, especially, soluble solid content (SSC) and firmness are among the major quality attributes of pears (Costa et al., 2002). Good-quality pears develop a buttery, juicy texture, following softening related to changes in cell wall structure (Murayama et al., 2006). Charting pH, SSC and firmness as a function of postharvest storage time could provide valuable information for commercial decision-making, since fruit sold to the consumer must meet given quality standards based on these parameters (Paz et al., 2009). Some published papers also had reported the application of Vis/NIR and NIR spectroscopy for predicting the internal quality of pear. Liu et al. (2007a,b) developed different models for predicting SSC and firmness of pear based on multi-linear regression (MLR), principal component regression (PCR) and partial least squares regression (PLSR). Research found that PLSR is the most reliable and robust model with r_p = 0.9121 and 0.8541, and RMSEP = 0.6691 and 1.2324 for SSC and firmness, respectively. Ying and Liu (2008) investigated NIR spectroscopic (800–2600 nm) techniques with partial least squares (PLS) and ge-

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netic algorithms (GAs) analysis for determining the sugar content (SC) (RMSEP = 0.395), titratable acidity (TA) (RMSEP = 0.0195) and valid acidity (pH) (RMSEP = 0.0089) of pear, respectively. Nicolaï et al. (2008) used continuous wave and time-resolved near infrared reflectance spectra (780–1700 nm) to determine the SSC of pear. PLS method was used to construct calibration model. The best prediction result was obtained for SSC with $r^2 = 0.60$ and RMSEP = 0.44. Paz et al. (2009) compared the performance of different spectrophotometers for predicting soluble solid content, firmness and postharvest shelf-storage time in intact pears. They found that a scanning monochromator (SM) of 400–2500 nm and a combination of diode array and scanning monochromator (DASM) of 350–2500 nm outperformed a diode array (DA) of 900–1700 nm based on the developed PLS model. Sun et al. (2009) used Vis/NIR spectroscopy to measure SSC of 'Cuiguan' pears on-line. PLS and LS-SVM were used to develop calibration models. The results showed that fruit moving speed has few effects on spectra and model performance at a fruit moving speed of 0.3–0.7 ms^{-1}. At 0.5 ms^{-1}, the best model for SSC was PLS regression coupled with original spectra. Hao et al. (2010) investigated Vis/NIR diffuse reflectance spectroscopy at 530–1560 nm region for the analysis of SSC of pear. The raw and pretreated spectra by wavelet compression were modeled using least squares support vector regression (LSSVR). The prediction result was obtained for SSC with $r = 0.93$. Xu et al. (2012) compared four variable selection methods (SMLR, GA-PLS, iPLS and GA-SPA-MLR) in the spectra range 533.13–929.81 nm. It was found that GA-PLS and GA-SPA-MLR models exhibited higher coefficients of determination $r^2 = 0.878$, 0.880 and RMSEP = 0.459, 0.457 for SC of the validation set, respectively.

However, the calibration methods in the literature stated above were almost PLS analysis (or more effective models were developed based on PLS method) or other linear analysis (e.g., MLR and PCR) and the wavelength region excluded the visible region which had a close relation to the color changes during pear growth. The color of fruit peel has some changes with degree of ripeness. This change may be why some researchers found models obtained by visible and near infrared spectroscopy (Vis/NIR) were better than models obtained by single NIR (Park et al., 2003; Paz et al., 2009). Therefore, combining both the visible region and near infrared region may be more helpful to develop reliable model for prediction of SSC, pH and firmness. In addition, the PLS model only discussed the linear relationship between the spectra and chemical components of pears, whereas, there might be latent nonlinear information related to the chemical constituents. Only a few studies have sought to apply nonlinear analysis for predicting the internal quality of pear. No hitherto-published research has dealt with simultaneous prediction of SSC, pH and firmness in different varieties of pears. In the present work, a new and promising machine learning method, least squares-support vector machine (LS-SVM) has been applied to develop the calibration models for the determination of SSC, pH and firmness in three varieties of pears. LS-SVM has the capability of dealing with linear and nonlinear multivariate calibration and resolving these problems (Yu et al., 2009; Zhu et al., 2010; Wu et al., 2012). Therefore, the present work was using visible and near infrared spectroscopy for the determination of SSC, pH and firmness of pears by LS-SVM with a comparison of PLS models.

The objectives of this study were (1) to investigate the feasibility of using Vis/NIR spectroscopy to predict the SSC, pH and firmness of different varieties of pears; (2) to compare the performance of different wavelength regions including visible region, NIR region and Vis/NIR region by PLS and LS-SVM analysis; (3) to achieve the best calibration models after the comparison of PLS and LS-SVM models; and (4) to confirm the effective wavelengths (EWs) of each property and evaluate the effectiveness of the EWs.

2. Materials and methods

2.1. Fruit samples

In the present work, a total of three varieties of pears were obtained in local market named Cuiguan, Huanghua and Qingxiang. All of these pears were common variety in China. In terms of peel color, Cuiguan pear variety is yellow-green in appearance, however, surface color of Huanghua and Qingxiang pear varieties are similar and exhibit yellowish-brown. The equatorial diameter range of pears was 70–80 mm, and all samples were individually washed, numbered and stored in standard refrigeration (2 °C). Before the experiment, samples were taken out from cold storage accommodation and placed under room condition (20 °C, 60% relative humidity) for more than 2 days to have an equalization room temperature. A total of 240 samples (80 for each variety) were prepared for further treatments. Seventy samples were selected randomly from each variety and a total of 210 pear samples were used in the calibration set, whereas, the remaining 30 samples (10 for each variety) were selected as the validation set for estimating the performance of models. No single sample was used in calibration and validation sets at the same time. In order to compare the performance of different calibration models, the samples in the calibration and validation sets would keep unchanged for all calibration models and this was set as a basic condition in this paper.

2.2. Vis/NIR reflectance spectroscopy collection

The experimental system for testing pear fruit included a spectrometer (QualitySpec®Pro (350–1800 nm), Analytical Spectral Devices, Inc., USA) with an external fiber-optic cable installed at the high intensity contact probe/A122300, a Si detector and an InGaAs detector for 350–1000, 1000–1800 nm, respectively, tungsten halogen lamp with 12 V Bulb/A350610 to provide light source. A white Teflon tile was used for white calibration before every measurement. The angle between the incident light source and the detector fiber was set to 45°. The fiber cable delivered the collected optical energy into the spectrometer, where it was projected onto a holographic diffraction grating. The grating was separated and reflected the wavelength components for independent measurement by the detectors.

The measurement system was arranged in reflectance mode for collecting Vis/NIR diffuse reflectance spectra from the peel and flesh of pear fruit. Pears were placed steadily upon the fruit holder, with the stem–calyx axis horizontal. The reflectance spectra from 350 to 1800 nm were measured at 1 nm interval with an average reading of 10 scans for each spectrum. Three separate spectral measurements were made at three marked locations on each sample around the equator (120°) of the fruit, avoiding any obvious surface defects (bruises, scars, etc.). The aim of three measurements is to decrease the error of operator and instrument, and avoid the influence from uneven firmness distribution in whole fruit. The average spectrum of these three measurements was used for calibration model. That is to say, a total of 30 scans were automatically averaged for each fruit. Finally, all spectral data were stored in a computer for further analysis.

2.3. SSC, pH and firmness analysis

In order to assess the real quality parameters of fruit, the SSC, pH and firmness (compression test) were determined using traditional destructive tests. Firmness was first measured with a 3.5 mm diameter Magness-Taylor (MT) probe, which was attached to a fruit sclerometer (Model: gY-1, hangzhou Huier Instrument, Co. Ltd., Hangzhou, China) with accuracy of ±0.1 N. The skin was