Computers and Electronics in Agriculture 71S (2010) S10–S14

Contents lists available at ScienceDirect

Computers and Electronics in Agriculture

journal homepage: www.elsevier.com/locate/compag

Nondestructive measurement of internal quality of Nanfeng mandarin fruit by charge coupled device near infrared spectroscopy

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ARTICLE INFO

Article history:
Received 18 September 2008
Received in revised form 25 August 2009
Accepted 12 September 2009

Keywords:
Near infrared spectroscopy
Charge coupled device
Interval partial least squares
Nanfeng mandarin fruit
Soluble solids content
Total acidity

ABSTRACT

The soluble solids content (SSC) and total acidity (TA) are the major characteristics for assessing quality and maturity of Nanfeng mandarin fruits. The feasibility of charge coupled device near infrared spectroscopy (CCD-NIRS) combining with effective wavelengths selection algorithm used to measure SSC and TA nondestructively was investigated. The effective wavelengths to SSC and TA were chosen by interval partial least squares (iPLS) in the wavelength range of 600–980 nm. The predictive ability of SSC model used PLS regression was improved with *r* of 0.92 and RMSEP of 0.65 °Brix using effective wavelengths of 681.36–740.51 nm, 798.60–836.19 nm and 945.52–962.75 nm. The TA model was simplified with *r* of 0.64 and RMSEP of 0.09% using effective wavelengths of 817.57–836.19 nm, 909.85–927.60 nm and 945.52–962.75 nm. The experimental results demonstrated that the CCD-NIRS technique combining with iPLS algorithm was a feasible method to measure SSC and TA of Nanfeng mandarin fruits nondestructively.

1. Introduction

Fruit quality is an important factor affecting its market value, transportation and storage requirements. Fruit quality indices consist of internal quality, such as soluble solids content (SSC) and total acidity (TA), and external quality, such as size and weight. To measure the external quality of fruit, many researches have been conducted leading to promising advancements. As a result, there are many types of fruit sorters based on size or weight of the fruit (Blasco et al., 2003; Leemans et al., 2002; Kondo et al., 2000). However, determining the internal quality of fruit is not as straightforward as external quality measurement. Internal quality of fruit is usually measured by destructive or invasive approaches which involved a considerable amount of manual work.

Quantitative spectroscopy has been greatly improved by use of a variety of multivariate statistical methods of partial least squares (PLS) and principal component regression (PCR) (Haaland, 1988; Haaland and Thomas, 1988a,b). PLS or PCR can easily treat very large data matrices, extracting the relevant part of the information and producing reliable but very complex models (Geladi and Kowalshi, 1986; Chu et al., 2004). Recently PLS was considered to be almost unaffected by noise, and therefore it was commonly stated that no feature selection at all was required (Thomas and Haaland, 1990). This attitude has changed, and therefore it has been widely recognized that a feature selection can be highly beneficial, since a double goal can be reached: improve the predictive ability of the model and highly simplify it (Leardi and Gonzólez, 1998; Borin and Poppi, 2005). The interval partial least squares (iPLS) is developed by Nørgaard et al., which searches for a spectral interval that is particularly informative with respect to the parameter under consideration (Pereira et al., 2008). The SSC and TA are two most important internal quality parameters of Nanfeng mandarin fruit. But SSC and TA determination are normally performed destructively on juice. Charge coupled device near infrared spectroscopy technique (CCD-NIRS) combining with chemometrics algorithms is a powerful tool, because of its fast detection and simple operation in sampling. NIRS technology has been used to determine SSC and TA in mandarin fruit (Gómez et al., 2006; McGlone et al., 2003; Liu et al., 2009), apple (Liu et al., 2007; Liu and Ying, 2005; Sánchez et al., 2003; Lu and Ariana, 2002; Lammertyn et al., 1998), tomato (Shao et al., 2007; André et al., 2005; Slaughter et al., 1996) and peach (Slaughter and Crisosto, 2006; Ying et al., 2005). Even if these instruments are highly accurate, their application to field research, such as monitoring chemical changes of developing fruits on trees, are limited by their large sizes and weights. CCD-NIRS sensor supplies the chance to develop portable or online operation, because its advantages of low cost, robust performance and small size. The charge coupled device (CCD) micro-spectrometers sometimes suffer from poor performance compared to conventional spectrometers but are perfectly suited for use with fiber optics (Davies et al., 2001). And some recent studies have illustrated the use of CCD micro-spectrometers for portable NIR applications.

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doi:10.1016/j.compag.2009.09.005

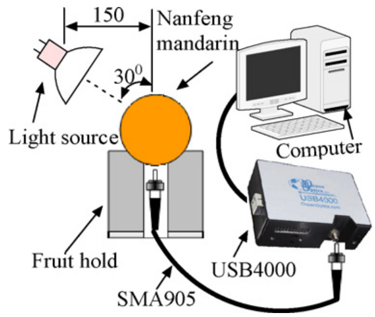

Fig. 1. Schematic of Nanfeng mandarin fruit CCD-NIRS acquisition device.

Saranwong et al. (2003) reported that the accuracy of the Kubota NIR instrument "Fruit Selector" was 0.40 °Birx in SEP for SSC value determination of intact mango. Temma et al. (2002) showed that the portable NIR instrument developed by their research center had excellent potential in determining SSC value of intact apples. Reita et al. (2008) evaluated variety compatibility of fruit to a NIR Brix calibration system of NIR-GUN (FANTEC, Kosar-city, Japan). Camps and Christen (2009) developed a portable NIR instrument for determining SSC, TA and firmness of apricots with a miniature optical component (S-2000).

The objectives of this study are to evaluate the feasibility of CCD-NIRS in nondestructive measurement of the SSC and TA in Nanfeng mandarin fruit. The prediction of calibration models were also compared in the manuscript.

2. Materials and methods

2.1. Nanfeng mandarin fruit

One hundred and fifty three Nanfeng mandarin fruit samples were harvested in a local orchard of Shishan, Nanfeng, China, in 10 October 2007 (latitude: 116.50; longitude: 27.23). After arriving laboratory, they were placed in airtight polyethylene bags and stored in an ice filled refrigerator to keep at cold temperature (4 ± 1 °C). All fruit samples were allowed to equilibrate to room temperature (20 °C) before NIRS measurement.

The sample composed of two varieties of Mandarin namely Daguoxi (77 fruits) and Xiaoguoxi (76 fruits). For increasing the application scope of models, Daguoxi and Xiaoguoxi samples were put together. Thus 153 fruit samples were used to establish the calibration models. However, because of chemical measurement errors, 4 and 13 samples were deleted as outliers for the SSC and TA calibration, respectively. The residual samples were divided into calibration and prediction sets, the statistical results were presented in Table 1.

2.2. System set up and transmission measurements

Fig. 1 showed the schematic of Nanfeng mandarin fruit CCD-NIRS acquisition system. The system consisted of a tungsten halogen lamp (24 V/50 W), CCD spectrometer (USB4000), an optical fiber (SMA905), USB data line and PC. The CCD spectrometer was 3648 pixel photodiode array. The wavelength range of the spectrometer was 350–1040 nm with a 0.2 sampling interval. Reflectance, interactance and transmittance modes compared by Nicolaï et al. (2007). The transmittance mode was applied, because the peel of mandarin was interference with determination internal quality precisely (Krivoshiev et al., 2000). The transmitted light carried information about the skin and core of the mandarin when the arrangement of 180° was applied, which might not be relevant to internal quality. Therefore an arrangement of about 30° was adopted between the lamp axis and the vertical line. The horizontal distance was about 150 mm between the center of lamp and fruit hold. And a similar system had been applied to determine SSC of intact citrus with RMSEP of 0.54% by Lu et al. (2007). Fu et al. (2007) detected brown heart of pear and Sun et al. (2009) investigated the effect of fruit moving speed on predicting SSC of 'Cuiguan' pear by the same similar arrangement.

NIR spectra were collected and transformed by OOIBase32 software (Oceanoptics Inc., Dunedin, USA), from three positions which were marked with a circle beforehand on each mandarin fruit around equatorial position. The averaged transmission reflectance spectrum of every mandarin fruit was analyzed with the statistical program for multivariate calibration of Unscrambler v9.5 software (CAMO AS, Trondheim, Norway).

2.3. SSC and TA reference analysis

SSC and TA were determined by traditional destructive tests. Each fruit unit was juiced, then SSC was obtained using a digital refractometer PR-101α (Atago Co. Ltd., Tokyo, Japan), TA was assessed by potentiometric titration of a 2 mL sample of juice and expressed as percentage of citric aid.

3. Results and discussion

3.1. Evaluation index of model

The performances of the PLS calibration model were evaluated in terms of the root mean square errors of cross validation (RMSECV), the root mean square errors of prediction (RMSEP) and the correlation coefficient (r). The RMSECV was calculated as follows:

$$E_c = \sqrt{\frac{1}{n_c - 1}\sum_{i=1}^{n_c}(\hat{y}_i - y_i)^2} \qquad (1)$$

where E_c is the RMSECV, $\hat{y}_i$ is the prediction value of the ith observation, y_i is the measured value of ith observation and n_c is the number of observation in calibration set.

For the prediction set, the root mean square error of prediction (RMSEP) is calculated as follows:

$$E_p = \sqrt{\frac{1}{n_p - 1}\sum_{i=1}^{n_p}(\hat{y}_i - y_i)^2} \qquad (2)$$

where E_p is the RMSEP, $\hat{y}_i$ is the prediction value of prediction set sample, y_i is the measured value of prediction set sample, and n_p is the number of observation in prediction set.

Table 1
Statistics of SSC and TA measured by the standard destructive methods for the calibration and prediction sets of Nanfeng mandarin fruit.

	Calibration set					Prediction set				
	Number	Average	Max.	Min.	S.D.	Number	Average	Max.	Min.	S.D.
SSC (°Brix)	107	14.00	18.00	11.20	1.68	43	14.00	10.50	18.00	1.64
TA (%)	104	0.44	0.81	0.23	0.08	42	0.45	0.75	0.22	0.07