

Online Evaluation of Yellow Peach Quality by Visible and Near-Infrared Spectroscopy

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Abstract: To evaluate the possibility of using visible and near-infrared spectroscopy for the determination of SSC, TSC, TAC and water content in yellow peach, 60 yellow peaches with different maturity were hand-harvested from an orchard in Suzhou city, China and spectral measurements were done with an ASD FieldSpec 3 Portable Spectroradiometer (The wavelengths range of 350-2500 nm), on 17 August 2011. In this study, the contents of internal quality with different maturity differ greatly; Total Sugar Content (TSC) is 3.828-26.37%, Total Acid Content (TAC) is 0.383-0.961%, Soluble Solids Content (SSC) is 9.1-12.9° Brix and water content is 81.211-90.752%. We analyzed the correlation between TSC, TAC, SSC and water content and the two indices of spectral data. These were the reciprocal-logarithm-transformed reflectance ($\log(1/R)$) and the first-order derivative of reciprocal-logarithm-transformed reflectance ($d\log(1/R)$). The results showed that the spectra of yellow peach had common spectral characteristics and the pattern of the absorption curves was similar to that for other fruits. The first-order derivative of reciprocal-logarithm-transformed reflectance ($d\log(1/R)$) showed stronger correlation for some wavelengths. These wavelengths with stronger correlation were selected for the sensitive wavelengths and were used for the model calibration based on Multiple Linear Regression (MLR). TSC, TAC, SSC and water content of yellow peach were predicted at each sampling point using the multiple line models. Overall, although the TAC determination still needs to be improved, the determination of TSC, SSC and water content in yellow peach fruits by ASD near-infrared spectral analysis (350-2500 nm) was still successful ($R^2 > 0.61$) and the corresponding RMSEs of 2.32, 0.44 and 0.85%, respectively, showing that the spectroscopy has the ability to rapidly and non-destructively determine the internal quality of yellow peach.

Keywords: Spectroscopy, SSC, TAC, TSC, water content, yellow peach

INTRODUCTION

China is the most important producer of yellow peach in the world. It is the country where yellow peach originated and it has grown in China for over 3000 years. Yellow peach has enough nutrient content and it is rich in antioxidants, dietary fibers and trace elements (such as selenium and zinc), which is directly beneficial to people's health. With the development of the living standard of the people, recently, the concern about fruit quality is growing all over the world and consumers are paying more attention to the internal quality attributes of fruits (such as flavors and sugar content etc.), so it is more necessary to develop fast and efficient techniques to accomplish fruit quality determination (Cen and He, 2007).

Compared with the traditional methods of chemical analyses, visible and near-infrared spectroscopy is a reliable, rapid, nondestructive, chemical-free technique, takes less time and is easily used in continuous fruit quality evaluation. Visible and near-infrared

spectroscopy includes the visible spectra that mainly contain the color information and near-infrared spectra that mainly correspond to C-H, O-H and N-H vibrations (Osborne, 2000). Spectroscopy has previously been used as a effective method to detect the Soluble Solids Content (SSC), Total Sugar Content (TSC) and dry matter content of fruits, such as the apple (Liu and Ying, 2005; Harker *et al.*, 2008), pear (Nicolaï *et al.*, 2008), grape (Cozzolino *et al.*, 2008, 2011), mango (Jha *et al.*, 2005), kiwifruit (Schaare and Fraser, 2000), orange (Cayuela, 2008), apricot (Chen and Zhang, 2006), jujube (Wang *et al.*, 2011), mandarin (Gómez *et al.*, 2006; Sun *et al.*, 2011), strawberry (ElMasry *et al.*, 2007), mulberry (Huang *et al.*, 2011). Moreover, there are also many researches on peach based on visible and near-infrared spectroscopy. For example, the best model for SSC and PH had a correlation efficient of 0.96, 0.95 and a standard error of prediction of 0.534, 0.124, a bias of 0.052, 0.018, respectively in honey peach (Liu and Ying, 2004); the study results indicated that independent component analysis was a



Fig. 1: Sampling and labeling of yellow peach, on 17 August 2011

powerful way for the selection of sensitive wavelength and spectroscopy incorporated to least squares-support vector machine was successful for the accurate determination of SSC and pH value in peach (Shao *et al.*, 2011). Although numerous research articles have been published on internal quality determination of many fruit cultivars, none has specifically targeted the yellow peach. Researches published are usually focused on the SSC and TSC of fruit, rarely involving Total Acid Content (TAC) and water content. Actually, acid content and water content also have a great effect on their qualities and flavors.

Based on visible and near-infrared spectroscopy, this study describes spectral characteristics of the yellow peach and gives the results of a correlation analysis between the quality parameters (TSC, TAC, SSC and water content) and two indices of spectral data. The objectives of the present study were to identify the effective wavelengths that have the maximum discriminatory capability and to derive a discriminant function using these wavelengths in quality determination of yellow peach.

MATERIALS AND METHODS

Sixty yellow peaches were used to evaluate and develop visible and near-infrared models for quality determination by means of reflectance spectra. All yellow peaches with different maturity were hand-harvested from an orchard in Suzhou city, China and every sample was labeled before spectroscopic measurement, on 17 August 2011 (Fig. 1).

Immediately after recording the spectrum, the quality parameters of yellow peach (TSC, TAC, SSC and water content) were determined in the following methods. After yellow peach samples were ground and filtered to juice, the TSC was measured by anthrone colorimetric method (first the soluble sugar of fruit is extracted and anthrone reagent is added, then the absorbance of mixture of soluble sugar and anthrone reagent can be measured by 721-spectrophotometer); the TAC was measured by the titration and which can be calculated by the concentration of standard alkali

solution consumed; The SSC was measured by an Abbebenchtop refractometer (Model: WAY-2S, Shanghai Precision and Scientific Instrument Co. Ltd., Shanghai, China). The refractive index accuracy is ± 0.0002 and the °Brix (%) range is 0-95% with temperature correction; the water content of yellow peach was measured by direct drying method.

Methods: Spectral measurements were done with an ASD FieldSpec 3 Portable Spectroradiometer. Before the actual measurement, the instrument was calibrated with a standard whiteboard. The probe was positioned at a distance of approximately 10 mm from the surface of the yellow peach. The average spectral distribution for each sample was the average of 30 scans which were made at three positions around the equator of the fruit, with 10 scans at each position. The wavelengths of instrument range are from 350 to 2500 nm. Over the region of 350-1000 nm, the spectral sampling interval was 1.4 nm with a wavelength width of 3 nm; whereas between 1000 and 2500 nm, the spectral sampling interval was 2 nm with a wavelength width of 7 nm.

The preprocessing was carried out using "ViewSpec Pro V5.6" (ASD, American). This study used two indices of spectral data, namely the reciprocal logarithm-transformed reflectance ($\log(1/R)$) and the first-order derivative of reciprocal-logarithm-transformed reflectance ($d\log(1/R)$). $d\log(1/R)$ was calculated by:

$$d \log(1/R(\lambda_i)) \approx \frac{\log(1/R(\lambda_{i+1})) - \log(1/R(\lambda_{i-1}))}{\lambda_{i+1} - \lambda_{i-1}} \quad (1)$$

where, λ_i , λ_{i+1} and λ_{i-1} were the wavelengths and $R(\lambda_i)$, $R(\lambda_{i+1})$ and $R(\lambda_{i-1})$ were the reflectances at these wavelengths, respectively.

The software packages for data analysis and representation included SPSS 13.0 and Microsoft Excel. The correlation coefficients (r) between the quality parameters and the indices of reflectance were used to judge the effectiveness of sensitive wavelengths.

Analysis methods: Multiple Linear Regression (MLR) is a commonly used calibration algorithm which is simple and easy to interpret. However it fails when variables are more than samples and is easily affected by the collinearity between the variables (Naes and Mevik, 2001). In this study the variable number of full visible and near-infrared spectra was larger than samples. Therefore, it was not possible to run MLR directly and the effective variable selection was necessary before MLR models establishment. Selected variables with less collinearity would be helpful to improve the MLR models. The optimal band combination was determined by the lowest value of predicted residual error sum of squares. The prediction

performance was evaluated by the correlation coefficients (r) and Root Mean Square Error (RMSE). The best model should be the one with the smallest RMSE and the largest r .

RESULTS AND DISCUSSION

Typical visible and near-infrared spectra of yellow peach is shown in Fig. 2. The pattern of the absorption curves is similar to that for other fruit such as orange (Magwaza *et al.*, 2012) although position and magnitude of the peaks are fruit specific. Note that we did not use the spectral range of 350-400 nm and 2350-2500 nm (Fig. 2) for next analysis because the noise within these region can distort the reflectance signals (Yi *et al.*, 2007). From the visible region (400-700 nm), a continuous decrease in absorbance with the minimum at 603 nm is observed. High absorbance observed at 676 nm is indicative of red absorbing pigments, particularly chlorophyll that gives the fruit its characteristically green color (Gómez *et al.*, 2006). After this peak, there is a very sharp drop in absorbance as the spectrum enters the near-infrared region. Gómez *et al.* (2006) estimated this drop to be 12-fold. From 720 to 910 nm, the absorbance spectrum stays relatively flat until a prominent peak centered at 978 nm appears. This peak is most probably due to water and arbohydrate since they absorb strongly at 970 nm (Williams and Norris, 1987; McGlone and Kawano, 1998; Williams and Norris, 2001). Other three peaks related to the strong water absorbance bands exist between 1200, 1450 and 1950 nm (Williams and Norris, 2001) and in yellow peach these water absorption peaks occur at 1190, 1454 and 1937 nm, respectively.

The results of the laboratory analyses are summarized in Table 1. Table 1 show that the contents of these four parameters with different maturity differ greatly; total sugar content is 3.828-26.37%, total acid content is 0.383-0.961%, soluble solids content is 9.1-12.9° Brix (%) and water content is 81.211-90.752%. We did 8 groups of correlation analysis based on the four quality parameters (TSC, TAC, SSC and water content) and the two indices of spectral data. Based on these analyses, we produced graphs of the correlations between each of the parameters and types of spectral data (Fig. 3 to 6).

The positive correlations between TSC, TAC and $\log(1/R)$ (Fig. 3 and 4) are in the visible and near-infrared regions (400-2350 nm) of the spectrum and the negative correlations between water content and $\log(1/R)$ is in the most of bands. There are no significant correlations between TSC, TAC, SSC, water content and $\log(1/R)$ for any wavelengths. For TAC and $d\log(1/R)$ (Fig. 4), the correlation coefficient is >0.5 for wavelengths 608, 619 and 702 nm, respectively and the

Table 1: The summary statistics on the quality parameters content in yellow peach

| Quality indexes | Range (%) | Mean (%) | Variation (%) |
|-----------------|---------------|----------|---------------|
| TSC | 3.828-26.370 | 10.516 | 13.855 |
| TAC | 0.383-0.961 | 0.607 | 0.015 |
| SSC | 9.100-12.900 | 11.360 | 0.715 |
| Water content | 81.210-90.750 | 83.725 | 2.229 |

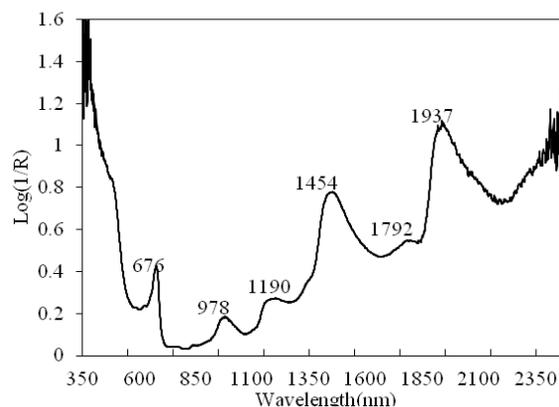


Fig. 2: A typical absorbance ($\log(1/R)$) spectrum of yellow peach in the wavelength from 350 to 2500 nm

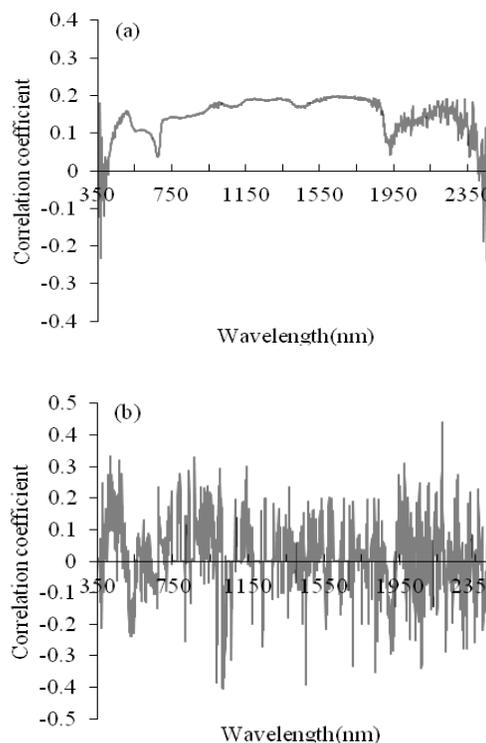


Fig. 3: Correlation between TSC and a $\log(1/R)$, b $d\log(1/R)$

wavelength with the strongest correlation is 619 nm with $r = 0.542$. For TSC and $d\log(1/R)$ (Fig. 3), there are the correlation coefficients >0.4 for two bands (1014 and 2174 nm, respectively). For SSC and $d\log(1/R)$ (Fig. 5), the maximum correlation wavelength is at 1705 nm with $r = 0.454$. Figure 6 shows that the

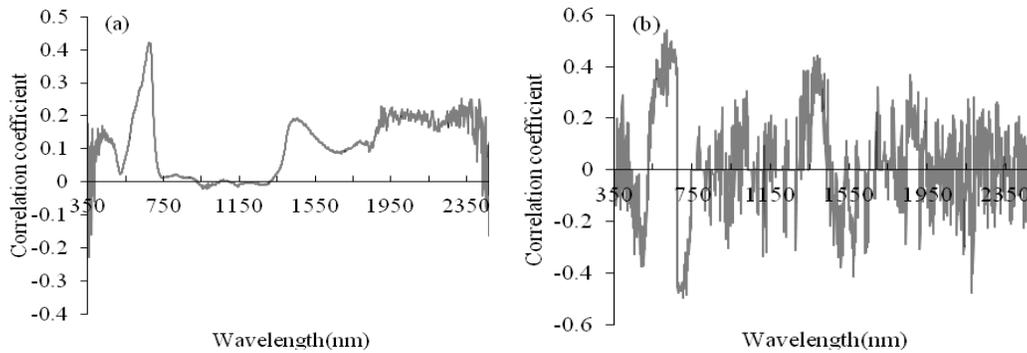


Fig. 4: Correlation between TAC and a $\log(1/R)$, b $d\log(1/R)$

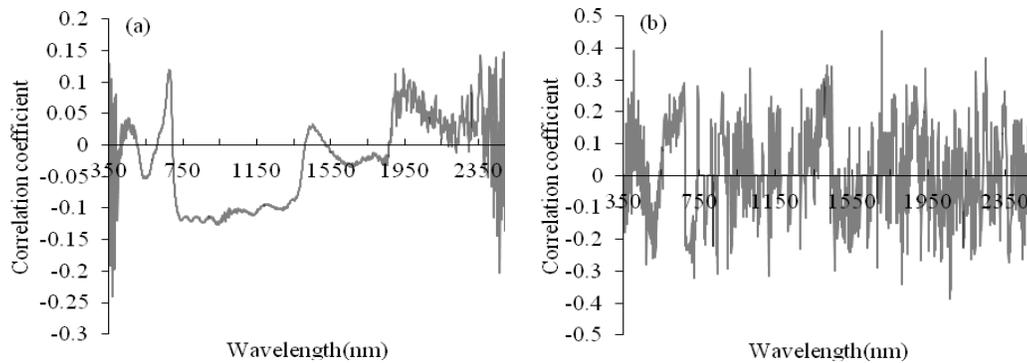


Fig. 5: Correlation between SSC and a $\log(1/R)$, b $d\log(1/R)$

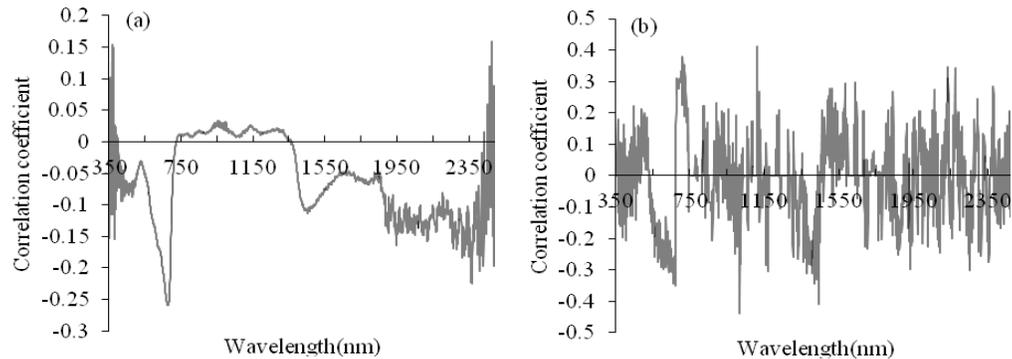


Fig. 6: Correlation between water content and a $\log(1/R)$, b $d\log(1/R)$

wavelength with the strongest correlation is 1017 nm with $r = -0.44$ for water content.

The sensitive wavelengths reflecting the characteristics of spectra for quality parameters were obtained based on correlation coefficients. After correlation coefficients were sorted between the quality parameters and the indices of reflectance (Fig. 3 to 6), the band with optimal correlation coefficient was selected first and suboptimum band was selected in turn in sensitive wavelengths analysis. In addition, the only peak band was selected in a interval with strong correlation, which was used to overcome the problem

of collinearity encountered with linear multivariate least squares regression models. According to existing experience rules, the ratio of the number of samples and variables is greater than or equal to 5 in MLR analysis (Shao *et al.*, 2011). So, the number of variables is not beyond 12 in modeling set of 60 samples. The selection results of sensitive wavelengths are summarized in Table 2. From Table 2, SSC and water content have same sensitive wavelengths such as 1017, 1112, 1933 and 2251 nm and similar sensitive wavelengths such as near 1420 and 1445 nm, respectively which shows that there is a relationship between water content and SSC.

Table 2: The selection results of sensitive wavelengths based on correlation coefficients

| Quality indexes | Sensitive wavelengths (nm) |
|-----------------|--|
| TSC | 420, 467, 866, 983, 1014, 1139, 1454, 1702, 1820, 1976, 2065, 2174 |
| TAC | 498, 570, 619, 702, 1112, 1318, 1387, 1442, 1510, 1572, 1863, 2176 |
| SSC | 408, 723, 1017, 1112, 1420, 1445, 1705, 1812, 1933, 2064, 2199, 2251 |
| Water content | 672, 711, 1017, 1112, 1169, 1379, 1419, 1442, 1933, 2133, 2173, 2251 |

Table 3: The calibration results of TSC, TAC, SSC and water content based on MLR with selected variables

| Quality indexes | LVs | r | RMSE (%) |
|-----------------|-----|------|----------|
| TSC | 10 | 0.78 | 2.32 |
| TAC | 7 | 0.74 | 0.08 |
| SSC | 10 | 0.85 | 0.44 |
| Water content | 9 | 0.82 | 0.85 |

LVs: The number of latent variables

From Fig. 1, water absorption peaks occur at 978, 1190, 1454 and 1937 nm in yellow peach. Therefore, the wavelength regions of 1400-1500 and 1900-2000 nm are affected by absorption related to water vapor. From Table 2, the absorption peak of TSC (866 nm) is associated with a third overtone stretch of CH and second and third overtones of OH around 700-900 nm which was referred by Rodriguez-Saona *et al.* (2001) in their article about rapid analysis of sugars in fruit juices by Fourier transform-NIR spectroscopy. Wavelengths below 700 nm were mainly attributed to the color or shape of yellow peach. Six hundred and twenty seven nm (Huang *et al.*, 2011) and 696 nm (Hong *et al.*, 2010) have been identified as a useful wavelength for the acidity of fruits determination, respectively, which are similar to the sensitive wavelengths of TAC (619 and 702 nm) in yellow peach.

The study makes full use of the advantages of MLR which is simple and easily interpreted and avoids the disadvantages of MLR. The selected variables were set as the inputs of MLR. The results are shown in Table 3.

For the prediction of TSC, therefore, MLR analyses using the first-order derivative of reciprocal-logarithm-transformed reflectance indicate that the wavelength combination (2174, 1014, 1454, 983, 1820, 2065, 1702, 420, 866 and 467 nm, respectively) are the most suitable for estimating TSC in the yellow peach. Compared with the other models, the linear model has the smallest RMSE (2.32 %) and the TSC derived from this model is strongly correlated with the measured TSC ($r = 0.78$).

From Fig. 7, the results indicate that the optimal method of prediction for TAC is with the model with 9 variables of the first order derivative of reciprocal-logarithm-transformed reflectance (Table 3). The results show that it is possible to predict TAC of the yellow peach from spectral measurements.

For the prediction of SSC, the ten-variables linear model has the smallest RMSE (0.44 %) and the SSC derived from this model is strongly correlated with the measured SSC ($r = 0.85$). And then, the water content of yellow peach can be also predicted from the first-order derivative of reciprocal-logarithm-transformed reflectance (RMSE = 0.85% and $r = 0.82$).

TSC, TAC, SSC and water content of yellow peach were predicted at each sampling point using the multiple line regression equations determined above (Table 3). The relationships between actual TSC, TAC,

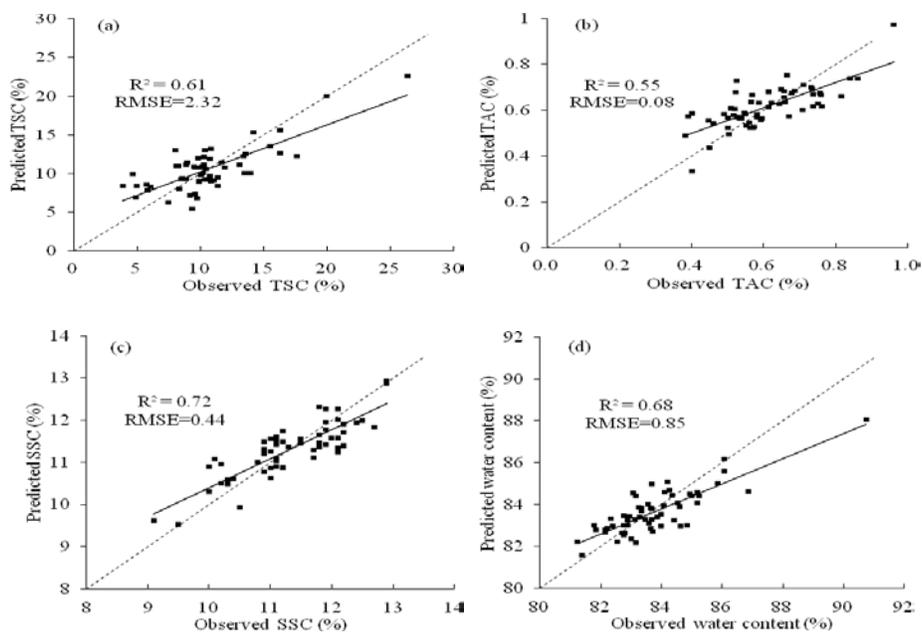


Fig. 7: Visible and near-infrared prediction results of 60 samples from the MLR models using the first-order derivative of reciprocal-logarithm-transformed reflectance for TSC (a), TAC (b), SSC (c) and water content (d)

SSC and water content and the predicted values were examined in terms of R^2 values, which are 0.61 ($p < 0.001$), 0.55 ($p < 0.005$), 0.72 ($p < 0.001$) and 0.68 ($p < 0.001$), respectively and the corresponding RMSEs of 2.32, 0.08, 0.44 and 0.85%, respectively (Fig. 7). In general, the $d\log(1/R)$ performs better than $\log(1/R)$ for predicting TSC, TAC, SSC and water content of yellow peach.

CONCLUSION

The correlation analysis with the two indices of transformed spectral data ($\log(1/R)$ and $d\log(1/R)$) showed no significant relationship between TSC, TAC, SSC and water content and the reciprocal-logarithm-transformed reflectance ($\log(1/R)$). However, the first-order derivative of reciprocal-logarithm-transformed reflectance ($d\log(1/R)$) showed stronger correlation for some wavelengths. These wavelengths with stronger correlation were selected for the sensitive wavelengths and were set as the inputs of multiple line regression analysis. TSC, TAC, SSC and water content of yellow peach were predicted at each sampling point using the multiple line models. The main conclusions of the research are as following:

Overall, the determination of TSC, SSC and water content in yellow peach fruits by ASD near-infrared spectral analysis (350-2500 nm) was successful. Although the TAC determination still needs to be improved.

Moreover, quality parameters of samples covered a large variety of different yellow peach (TSC: 3.828-26.37%, TAC: 0.383-0.961%, SSC: 9.1-12.9° Brix (%) and water content: 81.211-90.752%) in the study, showing that visible and near-infrared spectroscopy has the ability to rapidly and non-destructively determine the internal quality of yellow peach.

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