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Application of near-infrared spectroscopy to predict sweetpotato starch thermal properties and noodle quality^{*}

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Abstract: Sweetpotato starch thermal properties and its noodle quality were analyzed using a rapid predictive method based on near-infrared spectroscopy (NIRS). This method was established based on a total of 93 sweetpotato genotypes with diverse genetic background. Starch samples were scanned by NIRS and analyzed for quality properties by reference methods. Results of statistical modelling indicated that NIRS was reasonably accurate in predicting gelatinization onset temperature (T_o) (standard error of prediction $SEP=2.014$ °C, coefficient of determination $RSQ=0.85$), gelatinization peak temperature (T_p) ($SEP=1.371$ °C, $RSQ=0.89$), gelatinization temperature range (T_r) ($SEP=2.234$ °C, $RSQ=0.86$), and cooling resistance (CR) ($SEP=0.528$, $RSQ=0.89$). Gelatinization completion temperature (T_c), enthalpy of gelatinization (ΔH), cooling loss (CL) and swelling degree (SWD), were modelled less well with RSQ between 0.63 and 0.84. The present results suggested that the NIRS based method was sufficiently accurate and practical for routine analysis of sweetpotato starch and its noodle quality.

Key words: Sweetpotato, Starch thermal property, Noodle quality, Near-infrared spectroscopy (NIRS)

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INTRODUCTION

Sweetpotato (*Ipomoea batatas* LAM.) is among the world's most important, versatile, and under exploited food crops. With more than 133 million tons in annual production, sweetpotato currently ranks as the fifth food crop in developing countries after rice, wheat, maize, and cassava (Scott and Maldonado, 1999).

Though commonly categorized as a "subsistence" crop in most developing countries, sweetpotato's uses have diversified considerably in recent years. Diverse uses of sweetpotato have emerged in Asia, particularly in China, which produce 80% of the world's total output. Most of China's sweetpotato

output is used in livestock feed, but it is also processed into many food and industrial products. These include starch, sweeteners, noodles, citric acid, beverage and industrial alcohol, and ethanol fuel. Over 10% of the annual production of 100 million tons of sweetpotatoes in China is processed into starch, mostly in small-scale enterprises using manual or simple mechanized equipment. The starch is used mainly for noodle production, but food and other industrial uses are developing rapidly (Wheatley *et al.*, 1997).

Quality of many sweetpotato-processing products is affected by starch properties. Starch properties of interest include chemical, physical, pasting and gelatinization and so on. Among them, starch thermal properties measured by differential scanning calorimetry (DSC) have become more and more important recently. Starch gelatinization temperature is related to cooking time, starch granule size, and molecular size of the starch polymers and their

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relative amounts (Bao *et al.*, 2001). The starch thermal properties not only reflect starch gelatinization temperature, but also the heat energy input required for gelatinization, and the degree of starch gelatinization (Marshall, 1994). Gelatinization properties are directly responsible for starch industrial uses (Collado *et al.*, 1999). Besides, starch noodle processing quality is also very important for noodle processing industry, especially in China and Southeast Asia.

Sweetpotato starches have large genotypic variation in terms of their functional properties (Tian *et al.*, 1991; Lu, 2000; Collado *et al.*, 1999). Particular functional properties of individual starches are the keys to their commercial success. The possibility of breeding sweetpotato with tailored starch quality is attractive for its implication in expanding the range of sweetpotato-based products and the reduced use of industrial modification of sweetpotato starch for food use. However, screening a large number of early generation materials for starch properties through conventional analysis is time consuming and resource intensive. Breeding for improved starch quality is not practical unless a rapid and cost-effective screening method is available. In addition to the high cost, traditional methods of determining starch quality involve the use of hazardous chemicals.

Near-infrared spectroscopy (NIRS) technique is currently used in large-scale nutritional quality analysis of many crops (Wu *et al.*, 2002), as well as in starch analysis (Bao *et al.*, 2001). The main advantages of the NIRS technique are high efficiency, low cost and simultaneous quantification of several traits in one measurement. These advantages make it an ideal technique for large plant breeding programs where large numbers of samples in early generation need to be screened in a timely manner (Lu and Sheng, 1990). In rice, Bao *et al.* (2001) found strong relationships of NIR data with several important starch quality indexes including physiochemical quality, pasting and thermal properties, and believed that NIR analysis is sufficiently accurate for routine screening of large numbers of samples in early generation selection in rice breeding programs. Although NIR analysis in sweetpotato have been studied in dried flour (Lu and Sheng, 1990; Wu *et al.*, 1995; Ishiguro and Yamakawa, 1998) and fresh samples (Katayama *et al.*, 1996), application of NIR to analyze sweetpo-

tato starch thermal properties and noodle quality has not been reported so far.

The present research was aimed at establishing a rapid and accurate NIR based protocol for evaluating thermal properties and noodle quality in sweetpotato starch and at assessing its application potential in sweetpotato starch based food industry and its breeding for high quality starch.

MATERIALS AND METHODS

Starch sample preparation

A total of 93 sweetpotato genotypes including commercially released varieties and advanced breeding lines with diverse background were used in this study. All genotypes were grown at the experimental farm of Zhejiang University for varietal observational trial in 1999. Out of the 93 genotypes, twenty-one were selected based on the criteria described by Lu *et al.* (2003). These 21 selected genotypes were also planted in other 5 locations for multiple location trials in 1999.

Sweetpotato storage roots were harvested and starch was prepared for analysis within one week. Starch was isolated as follows: around 5 storage roots were cut into small rectangles that was crushed with 160 ml of running water for 90 s and sieved by 150- μ m mesh. Isolated starch was dried at room temperature and was further dried at 100 °C. Dried starch was ground with a model 3010-019 Cyclone grinder (Udy Corp., Fort Collins, Colo., USA). All dried starch samples were carefully kept in sealed, dried containers for further use.

Reference analysis of starch quality characteristics

The thermal properties of sweetpotato starch samples were analyzed with a DSC7 Modulated DSC thermal analyzer (Perkin Elmer PC Series, USA) equipped with DSC standard and dual sample cells. Sweetpotato starch (2.5 mg) was weighed into an aluminum pan into which 5 ml of distilled water was added; the pan was sealed with a lid and then heated at a rate of 10.0 °C/min from 40 °C to 110 °C. A sealed empty pan was used as a reference. Onset (T_o), peak (T_p), conclusion (T_c), T_r ($T_c \sim T_o$) and enthalpy (ΔH) of gelatinization were calculated automatically by Universal Analysis Program (Lu, 2003).

Starch noodle making quality was evaluated according to Chinese National Standard method described by Jin (1995). Starch noodle was prepared by using traditional preparation method. Carefully weighed 12 g of starch, put into a beaker, and mixed with 10 ml warm water (55 °C), and then stirred completely after adding 24 ml of boiling water. A further 108 g of starch and 52 ml of warm water were also added and stirred for 30 min at over 60 °C. Then the noodle was injected into boiling water by using a large injector. When noodles were floated, they were taken out, frozen for 12 h, and then thawed and air dried for evaluation. No additive was added during the whole procedures. *SWD*, *CL* and *CR* were used to evaluate the natural sweetpotato starch noodle quality. Five grams of 2.5 cm long noodles were taken and dried in an air forced oven at 105 °C for 4 h to determine dry matter content (m_1); the noodles were put into 100 ml boiling distilled water and heated for 15 min. After cooling, the wet noodles were weighed (m_2), and then air-oven dried at 105 °C for 4 h to determine dry matter content (m_3). *SWD* and *CL* can be calculated through the following formulas: $SWD = m_2/m_3$; $CL = (m_1 - m_3)/m_1 \times 100\%$. *CR* is defined as the broken noodle numbers among twenty 10 cm long noodles after cooling with 500 ml distilled water for 30 min.

All reference laboratory measurements were duplicated. These data were imported into the NIRS spectral data file, and used to develop calibration models. The 198 samples were sorted by reference data for each constituent, and every third sample was extracted for an external validation group (70 samples

total), so all samples were divided into NIR calibration set ($n=128$) and independent validation set ($n=70$) (Table 1).

NIRS analysis

NIR spectrometric analyses of sweetpotato starch samples were conducted according to the NIR standard procedures which include selection of calibration and validation samples, reference data obtained by routine laboratory analysis, NIR spectral data obtained by scanning samples, selection of optimum equations between spectral data and reference values by calibration, and finally confirmation of optimum equations by validation. The established prediction equations then were used to measure new independent samples.

1. Sample scanning

Sweetpotato starch samples were dried at 50 °C for 3 h to ensure that all samples had similar moisture content before NIR analyses. Spectral data were collected by measuring the diffuse reflectance from the starch sample in the NIR region within 1100–2500 nm, using a model 5000 monochromator equipped with a transport module (FOSS NIR Systems, Silver Springs, MD, USA). Each sweetpotato starch sample was scanned in duplicate in a small ring quartz with window cylindrical cell (NR-7073, internal diameter 35 mm, depth 9 mm). The reflectance spectra were collected continuously over a NIR wavelength region. It was necessary to use full spectral range for scanning because the parameters tested in this study consisted of a large number of physical, but few chemical characters. Each spectrum represented the average of

Table 1 Statistics of calibration and validation populations of sweetpotato starch thermal properties and noodle quality

Starch quality traits	Calibration ($n=128$)				Prediction ($n=70$)			
	Mean	SD	Min.	Max.	Mean	SD	Min.	Max.
DSC property								
T_c (°C)	83.84	1.44	79.53	88.15	83.89	1.50	79.57	88.21
T_o (°C)	68.05	4.42	54.79	81.31	67.27	4.82	52.80	81.74
T_p (°C)	75.89	3.12	66.54	85.23	76.06	2.92	67.32	84.81
T_r (°C)	16.55	5.73	7.07	33.75	17.09	6.20	8.34	35.68
ΔH (J/g)	13.68	0.49	12.20	15.16	13.60	0.58	11.85	15.35
Noodle quality								
<i>CL</i> (%)	8.91	1.08	5.67	12.14	7.82	1.13	6.32	11.72
<i>SWD</i> (g/g)	5.31	0.81	2.87	8.15	5.57	0.91	2.89	7.74
<i>CR</i>	5.05	3.27	0.95	14.85	6.71	4.27	1.21	19.52

32 scans, with the result recorded as $\log(1/R)$ at 2 nm increments. Duplicates of each sample were scanned twice (rotating the ring cup to a different position) to minimize the effects of particle size and sample temperature. The average spectrum of each sample was used for further analysis. The spectroscopic procedures and data recording were done using Win ISI II software (Version 1.04; FOSS NIR Systems, Silver Springs, MD Infrasoft International Inc., Port Matilda, Pa., USA).

2. Calibration and cross-validation

Calibration and validation were conducted following the manual of the Win ISI II software. Samples in the calibration set were used to establish multivariate equations between spectral data and laboratory reference values. Samples in the validation set were used to evaluate calibration equations. The NIRS instrument provides several mathematical treatments for calibration. Combinations of 1st and 2nd derivative, gap, smoothness and scatter correction were used to establish the best prediction equations. The optimum equations were developed in this study using modified partial-least-square (MPLS) regression on the first derivative of reflectance and transmittance spectra (math treatment, $D=1$, $G=4$, $S_1=4$, $S_2=1$), and scatter correction of SNVD (standard normal variance and de-trend) for starch quality parameters. D is the derivative order number (that is 0 indicates no derivative operation, 1 means the 1st derivative and so on); G is gap (the number of data points over which derivation is computed); S_1 is the number of data points in the 1st smoothing and S_2 is the number of data points in the 2nd smoothing which is normally set at 1 in the case of no 2nd smoothing. To calculate the relationships between spectral and physicochemical properties of the calibration samples MPLS regression analysis was performed using the full NIR spectra. This mathematical transformation reduced the original 300-plus and more variables (wavelengths) to a set of up to 16 orthogonal (MPLS) factors. Serving as regressors in the subsequent calibration step to build up the calibration function quantifying the relationships between spectral data and laboratory reference data (Shenk and Westerhaus, 1993). To prevent over fitting, this instrument provides cross validation to determine the optimum number of PLS factors. Three cycles of outlier elimination were set up with samples with an "H"

value (Mahalanobis distance) larger than 4 (spectral outlier) and a "T" value larger than 2.5 (sample which did not fit the calibration model) being eliminated (Shenk and Westerhaus, 1993). The accuracy of the calibration function was characterized by various NIR performance values. The best calibration equations were judged by the highest calibration RSQ (or statistic 1-variance ratio ($1-VR$) as an estimate of the coefficient of determination) and the lowest standard error SEC or $SECV$ (Wu et al., 2002).

3. Validation

To validate calibration equations, using cross-validation alone may not be sufficient. Samples independent from the calibration set were used to validate the initial calibration function, which led to subsequent NIR performance values for each constituent. The standard error of prediction and the determination coefficients can fully describe the NIR analytical error when analyzing samples of unknown quantitative composition (Lu and Sheng, 1990).

RESULTS

Spectral characteristics of sweetpotato starch

The spectral profiles of sweetpotato starch samples were determined and compared with those of sweetpotato flours which had been well studied in past few years (Lu and Sheng, 1990; Wu et al., 1995; Ishiguro and Yamakawa, 1998). Fig.1 shows that spectra between sweetpotato storage root flour and its starch were different. Although starch comprises approximately 70% of the total dry matter of sweetpotato

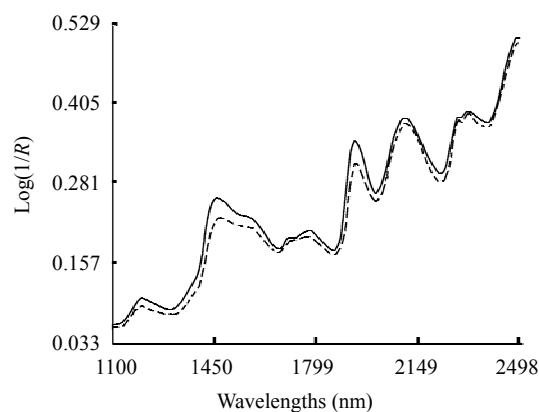


Fig.1 NIRS spectrum of sweetpotato flour and starch (Cultivar, Xu18; Starch: real line; Flour: broken line)

flour there are still large difference in their spectral characteristics, especially in long wavelength region. Obviously, it is impossible to use equations developed for sweetpotato flour constituents to estimate starch quality parameters. It is necessary to develop special equations for starch quality parameter measurement.

Variability of quality parameters of sweetpotato starch samples

The means, ranges, and standard deviations for each starch quality parameter of the 2 sets of sweetpotato starch samples (calibration set and validation set) are listed in Table 1. The wide range of variation in each set for each parameter suggested that two sample sets were representative of the overall genetic diversity in sweetpotato in terms of the starch quality parameters. The small differences in means, ranges, and standard deviations (*SD*) between the calibration set and the validation set demonstrated that the selected calibration set was suitable for NIRS calibration, and so was used as the validation set for validation.

Starch thermal properties

The calibration and validation statistics of the noodle quality parameters are summarized in Table 2. The *CR* equation is the most accurate $RSQ=0.89$, and an *SEP* of 0.528. The other equations developed were *CL* and *SWD* that had very low *RSQ* (only 0.63~0.70). NIR analysis of noodle quality of sweetpotato starch was only partially successful. The reason for that was most likely due to the relatively poor accuracy of the reference data. The *CR* is the most important noodle quality parameter (Jin, 1995), compared with the

other two parameters. Therefore, NIRS still has great potential to be used to predict sweetpotato noodle quality.

Noodle quality

The first attempt to get information correlated to rice starch thermal data by NIR (Shenk and Westerhaus, 1993) was only partially successful ($RSQ<0.74$). Similar work conducted by Bao *et al.* (2001) showed that although the T_c and ΔH of DSC profiles were poorly predicted, T_p and T_o achieved better prediction with low *SEP* and higher *RSQ*. The present study demonstrated that except T_c and ΔH , which were partially successful with a little low *RSQ* (<0.85), T_o , T_p and T_r could be determined by NIRS with acceptable accuracy ($RSQ>0.85$) (Table 2). Interestingly, T_r , which was identified as the most important DSC parameter for sweetpotato starch and noodle (Lu and Sheng, 1990) achieved very good prediction result. Therefore, predictions of main DSC parameters by NIRS are sufficiently accurate to be applied in sweetpotato quality breeding, especially for early selection phases of sweetpotato breeding. As far as we know, this might be the first report on the thermal parameters of sweetpotato starch by NIR.

DISCUSSION

The obtained NIRS performance parameters indicate high reliability of the estimation results for the principal quality constituents of sweetpotato starch (T_o , T_p , T_r and *CR*). The analytical accuracy is comparable to the applied reference methods. It is possible

Table 2 Calibration and validation of thermal properties and noodle quality of sweetpotato starch

Starch quality traits	Calibration		Prediction	
	<i>SEC</i>	<i>RSQ</i>	<i>SEP</i>	<i>RSQ</i>
DSC property				
T_c (°C)	0.633	0.898	0.991	0.838
T_o (°C)	1.952	0.886	2.014	0.853
T_p (°C)	1.224	0.879	1.371	0.889
T_r (°C)	2.278	0.888	2.234	0.862
ΔH (J/g)	0.227	0.904	0.421	0.840
Noodle quality				
<i>CL</i> (%)	0.754	0.755	0.932	0.632
<i>SWD</i> (g/g)	0.112	0.834	0.218	0.701
<i>CR</i>	0.249	0.903	0.528	0.887

to predict the content of other minor components (such as T_c , ΔH , CL and SWD) from NIR data with an accuracy that cannot be provided by other rapid screening methods used by the sweetpotato industry. For the latter group, NIRS can at least offer rapid qualitatively estimation in the initial screening stage of sweetpotato breeding.

The results can offer information accurate enough for sweetpotato breeders to select breeding lines with desirable starch quality properties. However, because NIRS analyses the sample indirectly, relying on calibration against results of reference analysis, the quality of the calibration processes critical for an accurate measurement of advanced breeding lines is poor. Therefore, certain amount of instrumental testing will still be needed to provide a reliable reference standard.

Previous reports showed that precision and reliability of NIR calibration and prediction could be affected by many factors, ranging from sample preparation to genetic variability of traits. Among these factors, accuracy of reference data is the most important factor affecting the precision of NIRS analysis most significantly. In the present study, the prediction equations for some starch parameters did not show satisfactory determination coefficients, especially for SWD and CL which had the lowest determination coefficient among all measured parameters. The lack of fit for these quality parameters can be explained by the lack of high quality reference data (Jin, 1995). Therefore, for developing satisfactory NIRS calibration of noodle quality, the method for generating high quality reference data must be further improved.

Application of NIRS to estimate main quality parameters in sweetpotato quality breeding, in particular, in screening for high dry matter and high starch content, and low amylose content, has been successfully attempted in several programs (Lu and Sheng, 1990; Katayama et al., 1996; Ishiguro and Yamakawa, 1998). In this study, some important starch quality parameters of sweetpotato starch samples have been determined by NIRS with good precision. As starch quality analysis by routine methods is often costly and time consuming NIRS provides sweetpotato breeders and starch enterprises with a simple, rapid and cost effective method for analysis of starch thermal properties and noodle quality.

In summary, the measurement of some quality parameters of sweetpotato starch can be accomplished with NIRS with a high RSQ (>0.85) and reasonable SEP . This level of precision is sufficient to allow breeders to screen new breeding lines for high starch quality and also to allow food enterprises to determine the various uses of sweetpotato starch. In order to improve calibrations, new sweetpotato starch samples with wide range of starch quality parameters should be added to this calibration population in future work. Further research will also be necessary to improve the accuracy of other starch quality parameters and also to transfer these calibrations to other instruments.

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