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Nondestructive determination of total and soluble solids in fresh prune using near infrared spectroscopy

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Abstract

A nondestructive optical method for determining the total solids content (TSC) and soluble solids content (SSC) of fresh whole prune (*Prunus domestica* L. 'French') was investigated. The method, based upon near infrared spectrophotometric techniques, could predict the TSC ($r^2 = 0.98$, SEP = 0.80% FW) and SSC ($r^2 = 0.96$, SEP = 1.02%) of prunes. A low cost ($2500 2002 USD) diode array-type spectrophotometer was used in the study.
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1. Introduction

In California, prunes, sometimes called dried plums, are produced from a limited number of European plum varieties that can be dried without fermenting at the pit. The French prune (*Prunus domestica* L. 'French') is the dominant variety. Fresh prunes are machine harvested in mid-August through mid-September and taken from the orchard to a local facility where they are dried with heated air in a truck-in-tunnel dehydrator (Thompson, 1981).

Grower payment is based on the quantity and size of the dried fruit. Size is officially based on the number of fruit per kg (USDA, 1965) but in practice is determined by estimating individual fruit weight based on its maximum diameter. A 18.2 kg sample of prunes is sized using a Dried Fruit Association of California (DFA) five screen grader. Undersized fruit, that passing a screen with 19-mm diameter holes, have no market value and the largest fruit, those retained on a screen with 23.8-mm diameter holes, have premium value. This system usually requires that a grower's fruit be maintained as an identifiable lot throughout drying and storage, which is more expensive than pooling the fruit before drying. It also causes growers' payments to be delayed until their fruit is completely dried and equilibrated in moisture, a process that takes 3–6 weeks.

A few drying operations in the past have mixed fruit from different growers during drying. This eliminates the cost of tracking an individual grower's fruit through the drying process and

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increases storage space utilization by eliminating partially filled bins. A lot of incoming fruit is weighed and a representative sample of fresh fruit collected and dried in a commercial tunnel. DFA size of the dried sample is then applied to the entire lot. However, growers do not have confidence in the fairness of this system and it has been abandoned (Dalrymple, 1996. Personal communication. Sunsweet Growers, Yuba City, CA).

Kader (1981) showed that the average dried weight of 50 fruit could be predicted ($r^2 = 0.81$) from average fresh weight. A system to predict dried weight was developed by Miller (1981) based upon fresh basis soluble solids concentration and fruit weight. The commercial implementation of this concept requires developing a fast, accurate and preferably nondestructive method of determining soluble solids concentration of the fresh fruit.

Near infrared (NIR) spectroscopy has been used as a rapid and nondestructive technique for measuring the internal quality of several commodities. For example, nondestructive NIR techniques for soluble solids content (SSC) determination have been demonstrated for several commodities including apple (e.g., Lammertyn et al., 2000), date (e.g., Schmilovitch et al., 1999), honeydew melon (e.g., Dull et al., 1992), kiwifruit (e.g., Slaughter and Crisosto, 1998), peach and nectarine (e.g., Slaughter, 1995), satsuma mandarins (e.g., Kawano et al., 1993), and tomato (e.g., Slaughter et al., 1996). NIR calibrations have also been developed for moisture content, dry matter or total solids content (TSC) in some intact commodities including date (e.g., Schmilovitch et al., 1999), kiwifruit (e.g., Slaughter and Crisosto, 1998), mango (e.g., Guthrie and Walsh, 1997), onion (e.g., Birth et al., 1985) and potato (e.g., Dull et al., 1989).

Traditionally, NIR methods have used either direct transmission or diffuse reflectance geometries. These techniques are applicable for samples with low light scattering and low optical density, samples where the optical path length can be adjusted to minimize the sample's optical density, or where the composition of the sample's surface is the same as its interior, or where the skin is sufficiently thin as to pose little interference in the signal. For example, Dull et al. (1989) were able to obtain satisfactory results using NIR transmission in their work on intact potato, Lammertyn et al. (2000) and Schmilovitch et al. (1999) were able to obtain satisfactory results using NIR reflectance techniques in their work on whole fruit. In some nondestructive applications, compositional differences between skin and interior prevents the use of diffuse reflectance when the sample is used in its natural, intact state and a high optical density prevents the use of direct transmission. Butler and Norris (1958) and Worthington et al. (1974) for example, have shown that the scattering and/or absorption of light transmitted directly through some types of intact produce can easily exceed 6 OD. Birth et al. (1984) found that reflectance measurements of papaya could not be used to distinguish immature from mature-green fruit, while interactance measurements were able to make this differentiation.

Interactance measurements (Conway et al., 1984) have been widely used for nondestructive applications of NIR in produce because with this method light enters the fruit and 'interacts' with the tissue inside and some of the unabsorbed light is internally reflected and is measured on the same side as the entrance beam (as in Fig. 1) allowing optical absorption spectrum to be collected from intact, optically dense biological specimens of irregular size such as fresh prune. A NIR spectrometer design for on-line measurement of sugar content in fruit has been developed by Bellon et al. (1993). Several commercial companies have developed or have NIR interactance-based produce

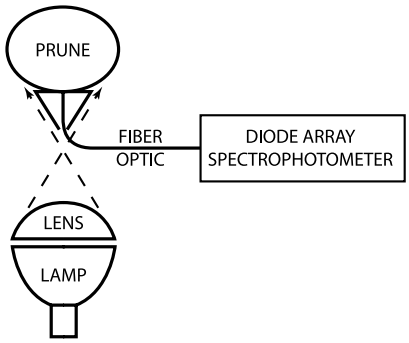

Fig. 1. Fiber optic configuration for light interactance measurements of intact prunes.

sorters at an advanced state of development which are capable of making on-line NIR spectral measurements at traditional commercial fruit sorting speeds.

This research studied the feasibility of determining fresh whole prune TSC and SSC with a nondestructive optical technique based upon NIR interactance.

2. Materials and methods

Three hundred fifty prunes (*Prunus domestica* L. 'French') were harvested in California over a two-week period, stored at 15 °C for a few days after harvest until ready to test and then equilibrated to room temperature (24 °C) for a few hours before evaluation. All fruit were defect-free and were rinsed in water to remove any surface dirt and then gently dried with a paper towel when removed from 15 °C storage. The optical absorption spectrum from 700 to 1100 nm was measured on each fresh prune using a custom interactance configuration developed for small fruit, Fig. 1. Each fruit was illuminated using an aspheric lens (model ASP 13310, JML Optical Industries, Inc., Rochester, NY) and halogen lamp (model 6465, Philips Lighting Co., Somerset, NJ) which produced an annulus of light on the fruit surface. The unabsorbed light emitted from the fruit was collected by a 1-mm bundle of 50-μm glass fibers (Schott-Fostec, LLC, Auburn, NY). The optical fiber was mounted in the center of an inverted conical metal platform with a base diameter of 15-mm that was located in the center of the annulus of illumination. A diode array spectrophotometer (model S1000-TR, Ocean Optics, Inc., Dunedin, FL) was interfaced to the fiber optic probe. The diode array spectrophotometer had a spectral resolution of 0.47 nm per diode and an optical bandwidth of 5 nm. A cylindrical Teflon® block, 50 mm in diameter and 22 mm thick, was used as the optical reference standard for the system.

To measure the optical absorption spectrum, each fruit was hand placed, with its suture plane horizontal, on the fiber optic probe so that the fruit was centered on and in direct contact with the probe. The absorption spectrum was measured on opposite sides of each fruit in a sequential manner and the two spectra were averaged to produce a single mean spectrum for each fruit.

Due to the destructive nature of the reference SSC measurement, the study was divided into two parts, one for SSC, and the other for TSC. This was necessary since the standard industry practice for TSC is to dry the whole intact prune (including the pit). One hundred of the 350 prunes were used in the SSC study and the remaining 250 were used in the TSC study. The SSC of a prune was determined following the spectral measurement using a temperature compensated refractometer (model RFM 100, Bellingham+Stanley Ltd., Atlanta, GA). The SSC was determined from the juice expressed from a portion of flesh cut from each side of each of the prunes in the SSC study at the same location where the optical measurements were made. Claypool et al. (1974) showed that there was little difference in French prune soluble solids measurements based on juice expressed from a portion of the fruit versus whole prune comminuted juice. The two soluble solids readings were averaged to determine the average SSC of the fruit. The volume of each prune in the TSC study was measured before drying, to allow density determination, using a pycnometer according to the method described by Bailey (1912) except that water was used in place of toluene and no vacuum was needed to remove air bubbles. The TSC was determined, following the spectral measurement, on each whole intact prune (including the pit) in the TSC study using a vacuum oven (model 29, Precision Scientific Co., Winchester, VA) according to the AOAC official method 920.151 (1999) and a temperature of 55 °C to avoid caramelization of the sugars. To allow correlation analysis between SSC and TSC, a 'without pit' TSC was determined from a second portion of tissue cut from each of the 100 prunes in the SSC study using the same AOAC method.

Prior to regression analysis, the spectral data were smoothed using the method described by Savitzky and Golay (1964) and then the second derivative was applied. Preliminary analysis using a trial and error process indicated that a second derivative segment of 6 nm and gap of 8 nm provided the best results. The second derivative

spectra, soluble solids and total solids readings were merged and a partial least squares (PLS, Martens and Naes, 1989) regression analysis was conducted using the NSAS software package (version 3.18, NSAS, 1990). To allow external validation of the calibration models the data sets were randomly split into 2 subsets of equal size with 50 observations for both calibration and validation of the SSC model and 125 observations for both calibration and validation of the TSC model (Neter et al., 1990).

Preliminary analysis using a trial and error process indicated that, for the electromagnetic region studied, the wavelength range of 750–1000 nm would provide the best results using the PLS multivariate calibration technique. The correct number of regression factors for the PLS model was determined by the minimum mean square error of cross validation, where the calibration data set in use was split into 5 subsets of equal size (Martens and Naes, 1989). Once a calibration model was developed it was used to predict the quality of the fruit reserved for external validation.

3. Results and discussion

The average and standard deviation values for the TSCs and SSCs in the calibration and validation data sets are shown in Table 1. The correlations between physical characteristics and the internal quality of prunes in the combined SSC data set are shown in Table 2. As expected, neither weight nor volume was highly correlated with either SSC or TSC. The density of the intact fresh fruit had a fairly high correlation with both SSC and TSC and SSC was highly correlated with TSC. The correlations between the physical characteristics and internal quality of prunes in the combined TSC data set are shown in Table 3. In this data set, fresh weight and volume had correlations in 0.7–0.8 range with dry weight as did dry weight and TSC. The density of the intact fresh fruit was also well correlated with TSC in this data set. Some of the differences between the levels of TSC correlations in Tables 2 and 3 may be due to the fact that the TSC in the SSC study was conducted on a subportion of the prune and did not contain the pit, while the value from the TSC study was conducted on the whole intact fruit including the pit, as is the standard industry practice.

The absorbance spectra for two intact prunes with a high and low TSCs and SSCs are shown in Fig. 2. The spectra of these two prunes after application of the second derivative treatment (6-nm segment, 8-nm gap) for baseline correction is shown in Fig. 3. The most apparent difference between the two spectra is at the 960-nm water absorbance peak. Williams and Norris (1987) have identified NIR absorbance bands for water (834, 938, 958, 978, 986, 994, 1010, 1030, and 1099 nm), sugar (838, 888, 913, 978, and 1005 nm), starch (878, 901, 918, 979, 1030, and 1053 nm), and cellulose (860, 905, 920, 978, and 1058 nm) that may account for the other differences observed between the two spectra.

A PLS calibration analysis was conducted to predict prune SSC. Cross validation indicated that a calibration model using 4 PLS factors was appropriate, $r^2 = 0.96$ and SEC = 0.93%, Table 4. Validation results for prune SSC were obtained from application of the calibration model to the remaining 50 fruit (Fig. 4). The validation data had a coefficient of determination of $r^2 = 0.96$, a SEP of 1.02% with a bias of 0.17%. These results

Table 1
Distribution of TSCs and SSCs of prunes in the calibration and validation data sets

Parameter	Data set	Samples	Mean	Standard deviation
Total solids	Calibration	125	28.3% FW	5.6% FW
Total solids	Validation	125	27.1% FW	5.6% FW
Soluble solids	Calibration	50	26.6%	4.9%
Soluble solids	Validation	50	25.0%	4.8%

Table 2
Correlation coefficients[a] between prune physical properties for combined SSC data set

	Fresh weight[b] (g)	Volume[b] (ml)	Density[b] (kg/m^3)	SSC[c] (%)
Volume[b] (ml)	0.997			
Density[b] (kg/m^3)	0.322	0.251		
SSC[c] (%)	0.499	0.443	0.851	
TSC[c] (% FW)	0.489	0.423	0.886	0.944

[a] All the correlation coefficients presented in this table are significant at the $\alpha = 0.01$ level.
[b] Determined on the fresh whole intact fruit.
[c] Determined from slices of prune that included the skin and flesh, but not the pit.

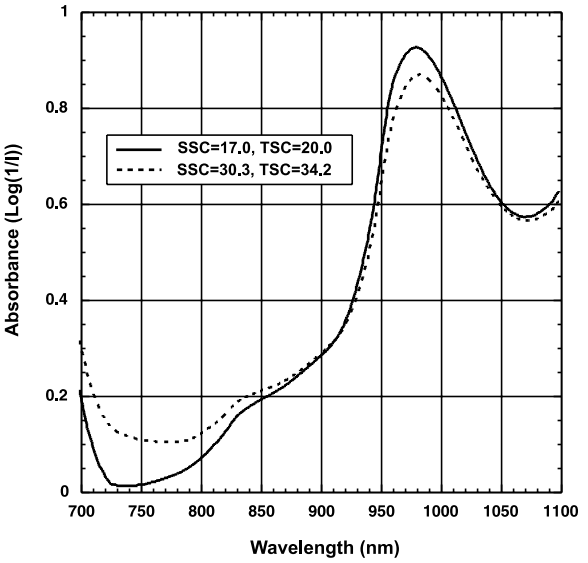

Fig. 2. Absorbance spectra of two intact prunes with high and low TSC and SSC.

indicate that use of 4 PLS factors did not lead to overfitting and that the calibration model for prune SSC appeared to be valid.

A PLS calibration analysis was conducted to predict prune TSC. Cross validation indicated that a calibration model using 5 PLS factors was appropriate, $r^2 = 0.98$ and SEC = 0.84% FW, Table 4. Validation results for prune TSC were obtained from application of the calibration model to the remaining 125 fruit (Fig. 5). The validation data had a coefficient of determination of $r^2 = 0.98$, a SEP of 0.80% FW with a bias of 0.14% FW. These results indicate that use of 5 PLS factors did not lead to overfitting and that the calibration model for prune TSC appeared to be valid.

The ratio of the standard deviation of the sample population divided by the standard error of performance of the NIR model (RPD) has been defined (Williams and Norris, 1987) as a measure of model performance. The RPD values for the TSC and SSC models are shown in Table 4. The RPD value can be used to assess the performance of the NIR calibration. For example, we can determine the percent of prunes that can be segregated into two groups, those with a TSC level below and those above the Tth percentile,

Table 3
Correlation coefficients[a] between prune physical properties for combined TSC data set

	Fresh weight[b] (kg)	Volume[b] (L)	Density[b] (kg/m^3)	Dry weight[c] (kg)
Volume[b] (l)	0.995			
Density[b] (kg/m^3)	0.112	0.017		
Dry Weight[c] (kg)	0.782	0.721	0.654	
TSC[c] (% FW)	0.146	0.057	0.929	0.718

[a] All correlation coefficients > 0.112 presented in this table are significant at the $\alpha = 0.05$ level.
[b] Determined on the fresh whole intact fruit.
[c] Determined on the dried fruit including the pit.

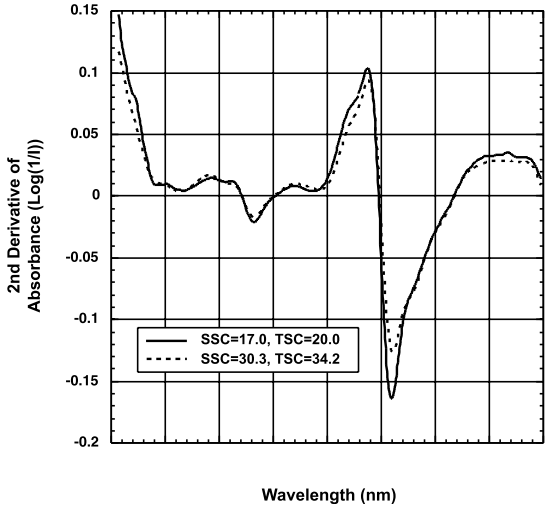

Fig. 3. Second derivative spectra of the same two intact prunes shown in Fig. 2.

with a level of confidence K using tabulated values for the probability of the standard normal deviate, Z (Steel and Torrie, 1980) as shown in Eq. (1).

$$P\left(Z < Z_T - \frac{Z_K}{\mathrm{RPD}}\right) + P\left(Z > Z_T + \frac{Z_K}{\mathrm{RPD}}\right) \qquad (1)$$

where Z_T is the standard normal deviate associated with the sorting threshold set at the Tth percentile, and Z_K is the standard normal deviate associated with the interval about Z_T due to the error in the NIR measurement that provides the level of confidence K in sorting accuracy.

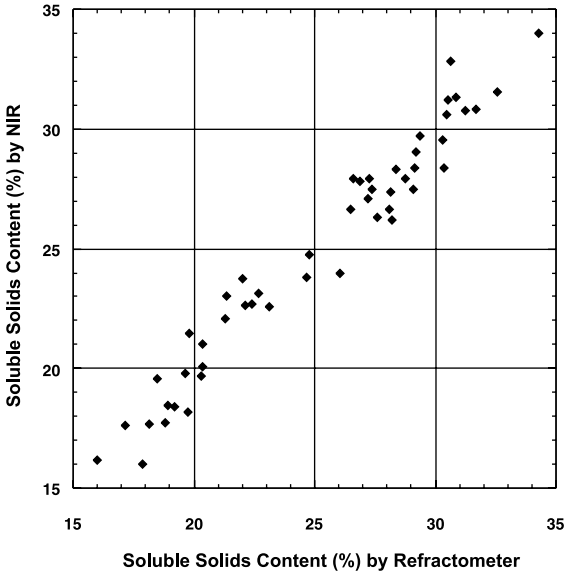

Fig. 4. Validation results for nondestructive prediction of SSC.

From Table 4 we have RPD = 7 for TSC. If we let $T = 10$th percentile, and $K = 95\%$ confidence level, Z_T and Z_K can be found as follows:

$P(Z < Z_T) = 0.10$ gives $Z_T = -1.28$ and,

$P(Z > Z_K) = 0.05$ gives $Z_K = 1.645$ thus from Eq. (1) we have,

$$P\left(Z < -1.28 - \frac{1.645}{7}\right) + P\left(Z > -1.28 + \frac{1.645}{7}\right)$$
$$= P(Z < -1.515) + P(Z > -1.045) = 0.92$$

Thus 92% of the prunes can be classified with this NIR model into two TSC groups, those below

Table 4
Summary of NIR calibration and validation performance for nondestructive internal quality assessment of French prunes

Parameter	Calibration				
	PLS factors	# Samples	r^2	SEC	RPD[a]
Total solids	5	125	0.98	0.84% FW	6.7
Soluble solids	4	50	0.96	0.93%	5.3
	Validation				
	# Samples	r^2	SEP	Bias	RPD[a]
Total solids	125	0.98	0.80% FW	0.14% FW	7.0
Soluble solids	50	0.96	1.02%	0.17%	4.8

[a] RPD, ratio of standard deviation (from Table 1) to standard error (from Table 4).

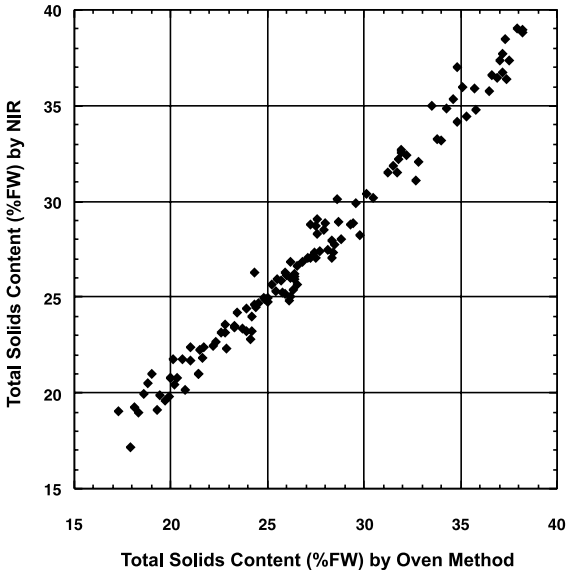

Fig. 5. Validation results for nondestructive prediction of TSC.

and those above the 10th percentile, with a 95% level of confidence for a TSC model with an RPD of 7.

In addition to the advantages of speed and nondestructive measurement, the NIR measurement is efficient since both TSC and SSC can be determined in a single step from the same spectral measurement of the fruit. If combined with the use of modern high-speed fruit weighing machinery, NIR-based TSC and SSC measurement could allow more complete prune quality determination based on fresh fruit measurements. This may allow fruit pooling at the dryer, faster grower payment and eliminate the overvaluing of small fruit caused by the DFA size grader described by Chalfant et al. (1999). It will also allow growers to predict the grade of their dried fruit based on fresh fruit characteristics and the immediate feedback provided by an NIR measurement will allow growers to better time harvest to optimize the value of their crop. Prune dehydrators could use the NIR measurement to determine the cost of dehydration related to the amount of moisture required to be removed from the fruit.

4. Conclusions

NIR spectroscopic techniques can be used to nondestructively and rapidly determine the TSC and SSC of prunes. The NIR measurement is conducted on the fresh whole prune and could eliminate the lengthy delay incurred with the current dehydration and moisture equilibration process used to determine fruit quality. The technique is also suited for use as the basis for an automated sorter where the fruit could be sorted into categories by SSC or TSC.

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