Starch and sugar – the assessment of maturation and ripening of fruit by shortwave near infrared spectroscopy

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Introduction

The "Herschel", or shortwave near infrared (SWNIR), region of the spectrum is used in the assessment of intact fruit, given relatively low absorption coefficients in this region, and the applicability of cheap (Si) detectors. For some fruit (e.g. mango), handheld SWNIR devices can be used in the field to assess fruit maturity, as indexed by fruit % dry matter content (DM) (an index of the total carbohydrate store in many fruit).[1,2] Also, SWNIRS can be used to assess fruit eating quality as indexed by total soluble solids content (TSS) either directly, or via measurement of total carbohydrate content (with starch converting to sugar during ripening).[1,2]

Zude[3] reported excellent calibration model statistics for the concentration of individual soluble sugars (glucose, sucrose and fructose) in banana mesocarp tissue for a PLS model based on diffuse reflectance spectroscopy of intact fruit using an extended visible-SWNIR (VIS-SWNIR) wavelength window (350–1700 nm) (e.g. for glucose: correlation coefficient of determination of

Figure 1. Handheld unit with mango fruit.

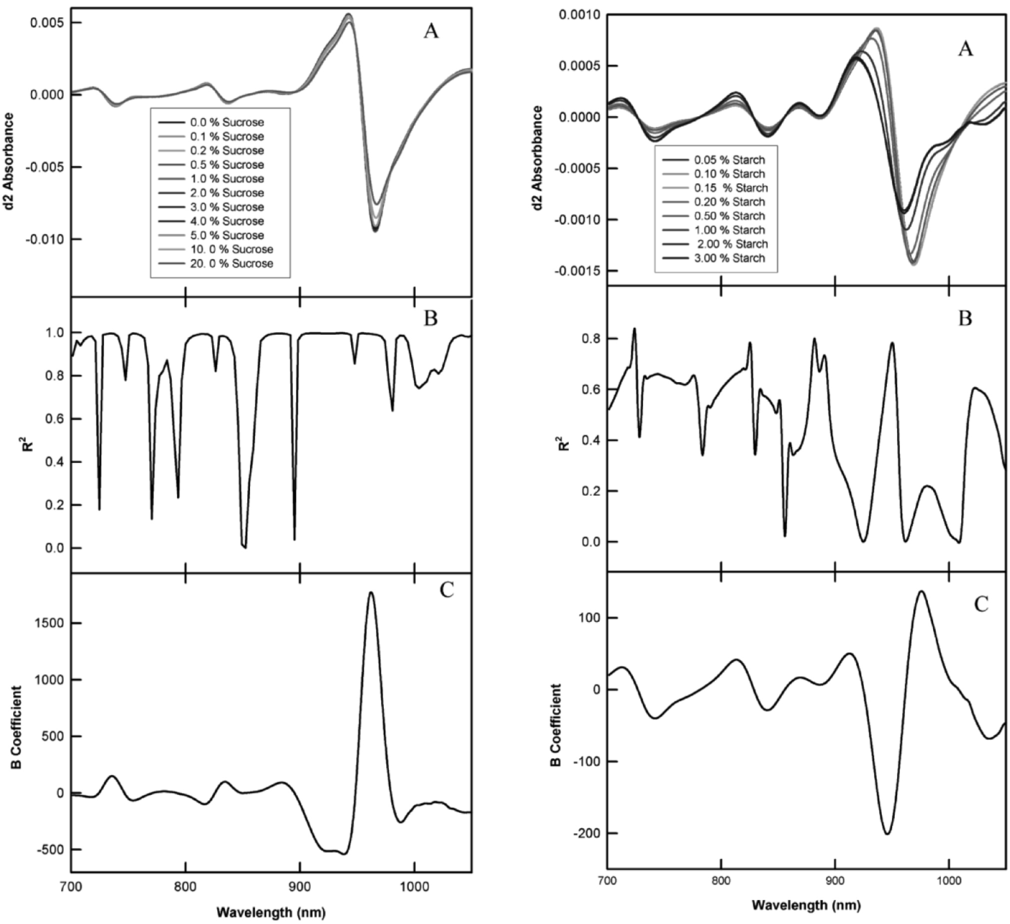

Figure 2. Sucrose (left panel) and starch (right panel) in solution, water as reference. Second derivative absorbance spectra of various levels of sucrose in water (0 to 20% w/v) and starch in water (0 and 3 % w/v) (Panel A), correlation coefficient of determination of cross-validation (R_{cv}^2) between absorbance at each wavelength and sucrose or starch levels (Panel B) and partial least squares regression model coefficients (Panel C).

cross-validation (R^2) = 0.96, root mean square error of cross-validation ($RMSECV$) = 1.8). It was concluded that VIS-SWNIRS could be used for non-destructive prediction of the "maturity" (ripeness) and quality of intact banana fruit based on determination of chlorophyll and sugar content. These results were encouraging, but the degree of correlation between individual sugars, or between individual sugars and other attributes (e.g. peel colour) was not reported. Thus it is not clear whether the sugars were assessed "directly" in the models developed, or indirectly through the relationship of an individual sugar to another attribute. In contrast, while McGlone *et al.*[4] reported accurate prediction of DM content of Royal Gala apples using SWNIRS at any stage of fruit ripeness, it was noted that prediction of TSS was poor before full fruit ripening.

It was considered that SWNIR spectroscopy may be appropriate for estimation of total carbohydrate content of intact fruit, but may not be capable of assessing component carbohydates, e.g. soluble sugar in ripening fruit, in which the starch/sugar ratios are changing. In this exercise, the ability to distinguish sucrose from starch in aqueous solution using SWNIRS was also assessed as a model system, and then the ability to measure soluble sugar in ripening mango, in which starch content is changing, was assessed.

Materials and methods

A Nirvana spectrometer (Integrated Spectronics; halogen lamp, 400–1100 nm wavelength range, approx. 10 nm wavelength resolution, repeatability [*SD* of repeated white tile measures] of approx. 1 mA; Figure 1) was used to acquire spectra of sugar, starch and sugar-starch solutions (transflectance across a 27 mm cuvette) and interactance spectra of intact mango fruit.[2]

Spectra were acquired of a set of 30 fruit on different days during the ripening process, by applying the interactance sensor directly to the surface of the fruit. PLS models were based on the second derivative of absorbance data.

Results and discussion

For many fruit, starch is converted to soluble sugars during the ripening process. Fruit %DM (mainly total carbohydrate content) was successfully predicted in fruit of different ripening stages using SWNIR (e.g. $R^2 > 0.88$ for mango fruit) (Table 1).

Soluble sugar content was modeled well in ripened fruit only (in which the conversion of starch to sugar is completed; (data not shown), and the technique was compromised when used across fruit of different ripening stages ($R^2 < 0.03$ for mango fruit) (Table 1). Use of the visible region improved calibration model performance (data not shown), but this was interpreted as an indirect assessment, with TSS content highly correlated ($R^2 > 0.85$) with skin colour. This relationship is not likely to be robust across different ripening or growing conditions.

As expected, Herschel absorption spectra of pure, "model" aqueous solutions of sucrose or starch were dominated by features relevant to vibration of the O-H bond, at around 740 nm, 840 nm and 970 nm, with the frequency of this vibration increasing (absorption band shifted to shorter wavelengths) as H-bonding decreased [e.g. with temperature increase or addition of solute (Figure 2)]. Both

Table 1. Prediction statistics for TSS and DM SWNIR models created using mango fruit of different ripening stages to that of the prediction set.

Character	Calibration sets	Prediction sets	Mean	SD	R_p^2	Bias
TSS	Days 1 to 8 Days 0–1, 6–8	Day 0 Day 3	5.1 6.4	0.36 1.24	0.01 0.03	1.10 0.78
DM	Days 1 to 8 Days 0, 1, 4 to 8	Day 0 Day 3	19.3 19.0	0.87 1.61	0.88 0.94	0.80 0.07

Table 2. Calibration cross-validation *RMSECV* statistic for sucrose and starch in pure aqueous solutions and in starch-sucrose mixtures (first column with optimal # factors, second column with fixed # factors).

		Pure solution	Sucrose/starch mixture	
Sucrose	Mean	4.6	3.93	3.93
	SD	6.04	5.76	5.76
	# Factors	1	5	2
	RMSECV	0.88	0.73	4.49
Starch	Mean	0.79	0.81	0.81
	SD	1.05	0.90	0.90
	# Factors	1	3	2
	RMSECV	0.39	0.06	0.15

the R^2 values for individual wavelengths and the SWNIR PLSR model coefficients were notably different for the sucrose and starch models, a result that might be due to different absorption characteristics of the two carbohydrates, or to light scattering by starch grains. Indeed, SWNIR model accuracy for starch concentration was not greatly impacted by varying sucrose solution. However, PLSR model accuracy for sucrose concentration was impacted by varying starch levels (*RMSECV* increased for models with a given number of PLS factors, Table 2).

Based on these results, SWNIR spectroscopy is recommended for assessment of DM, but not soluble sugar concentration, across ripening stages of fruit. Handheld SWNIRS has proven useful for the assessment of fruit maturity over time on a tree, within a tree, within an orchard (identifying maturity zones on farm), and in the packhouse for quality control on incoming lots.

References

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