Spectroscopic and chemometric analysis of short-wave near infrared spectra of sugars and fruits

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Introduction

Fruit sweetness, as indexed by total soluble solids (TSS), is a key factor in the description of fruit eating quality. Analysis using near infrared (NIR) spectroscopy can be based on pure statistical methods, but knowledge of the basic band assignments for the compounds of interest is advantageous. Previous considerations of this topic have focussed on the 1100–2500 nm spectral region.[1–5] Given the requirement for speed of assessment and the consequent use of Si diode array hardware in fruit sorting applications, a further consideration of band assignments in the short-wave NIR (SW-NIR) and the effect of changes in sample environment is warranted. A combination spectroscopic and chemometric approach has been adopted, following that of Maeda *et al*.[6,7]

Materials and methods

Sucrose, D-glucose and D-fructose were of analytical grade (BDH). Deuterium oxide of 99.93% isotopic purity was obtained from the Australian Nuclear Science and Technology Organisation. NIR spectra (400–2500 nm) were collected in triplicate for each sample, at each temperature (15–50°C, with 5°C increments) using a scanning spectrophotometer (model 6500, NIRSystems Inc, Silver Spring, MD, USA), equipped with a transmittance detector and a transport module with temperature controlling unit. A pathlength of 26 mm and an average of 32 scans were used for spectral acquisition. An empty cuvette was used as a reference. NSAS v. 3.30 software was employed for data collection and the Unscrambler v. 7.6 for the regression analysis. GRAMS32 v. 5.2 and kg-2d softwares were used for the production of the two-dimensional spectra.

Results and discussion

Spectroscopic analysis

NIR spectra of sugar solutions

Water OH groups display strong absorbances at around 750 and 960 nm in the SW-NIR spectral region (third and the second overtone bands of OH stretching vibrations). Sugar OH groups resonate at similar frequencies. The OH peaks of sugar solutions are better distinguished in deuterated water (for sucrose, Figure 1), with peaks at 740, 960 and 980 nm. The broad band at around 910 nm belongs to the third overtone of the sucrose CH stretching vibrations.
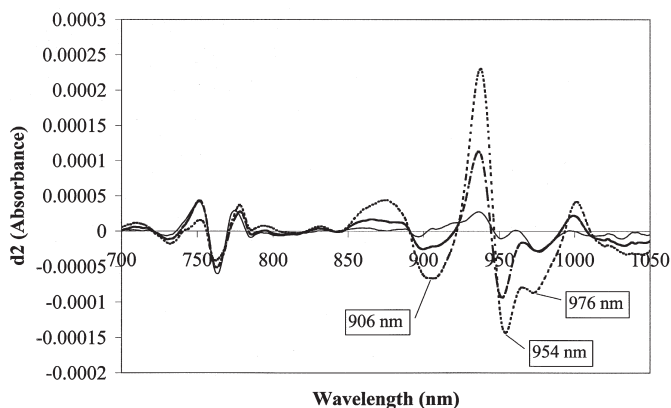
Figure 1. Second derivative spectra of sucrose solutions in deuterated water. — D$_2$O, –·– 20% sucrose and --- 50% sucrose.

The effect of temperature on the spectra of aqueous sugar solutions

Shifts of the water OH bands towards lower wavelengths upon increasing temperature conditions have been explained by the alteration in the structure of water and degree of hydrogen bonding.[6,8–12] At higher temperatures, singly hydrogen-bonded water molecules predominate. At lower temperatures, higher levels of hydrogen bonding occur, with vibration bands broadened and shifted towards longer wavelengths.

The spectra of the sugar solutions followed the same trend as the spectra of water, with bands at 750, 840, 960 and 985 nm slightly shifting towards shorter wavelengths and narrowing in bandwidth with increasing temperature. These bands appear as temperature-sensitive bands in the 2D spectra (Figure 2).
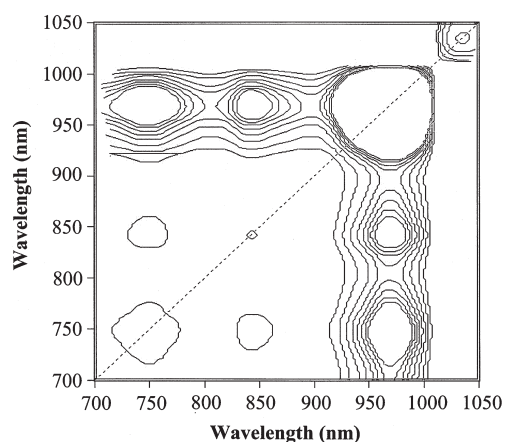

Figure 2. Influence of temperature variation (15–50°C) on the second derivative spectra of 50% sucrose solution.

The effect of concentration on the spectra of aqueous sugar solutions

Increase in sucrose concentration caused a decrease in the intensity of the large 964 nm band (second overtones of water–OH stretching vibrations) and an increase in the intensity of the smaller band at 982 nm (second overtones of sugar–OH stretching vibration) (Figure 3). The position of the 982 nm peak was moved towards higher wavelengths in more concentrated solutions.

Chemometric analysis

Prediction of temperature for aqueous sugar solutions

Temperature of 20% sugar solutions was predicted using the SW-NIR absorbance spectra.
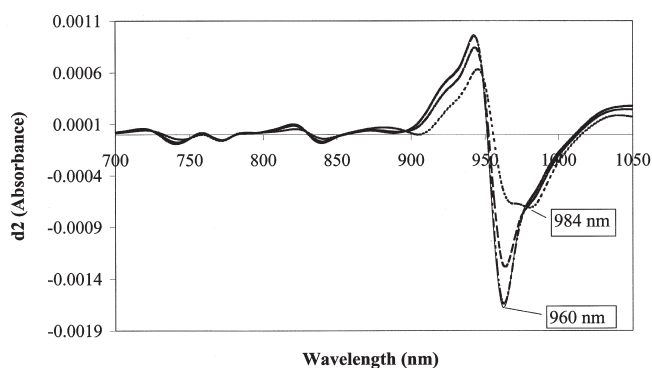
Figure 3. Influence of concentration variation (0, 5, 20 and 50%) on the second derivative spectra of sucrose solutions at 30°C. (— H$_2$O, –·– 5% sucrose, – – – 20% sucrose, ---- 50% sucrose).

The largest positive PLS1 B-coefficients were placed at 940 and 980 nm, with two other areas of positive coefficients at 750 and 840 nm, consistent with temperature sensitivity of the OH associated vibrations, related to the degree of hydrogen bonding.

Calibration on aqueous sugar concentration

PLS1 calibrations on sugar concentration exhibit high correlation coefficients (for example, at 30°C: R^2 0.989 in all cases, described with *ca* two PLS factors). The largest B-coefficients were placed at about 910 nm, consistent with third overtone bands of sugar–CH vibrations. Other positive B- coefficients were found in the region of 750–820 nm for sucrose and as two partially overlapped sets (750–770 and 790–820 nm) for D-glucose and D-fructose. As the latter regions are affected by temperature, it is to be expected that a calibration for sugar concentration, built across a range of temperatures, will downweight the coefficients in these regions. Indeed, PLS calibrations on concentration for the three sugars (Table 1) developed across a range of sample temperatures (with temperature treated as an *x*-variable) demonstrated a reliance on the 910 nm band (temperature insensitive CH stretching band). Negative coefficients at 840 nm, present in a single temperature calibration, were not present.

Explaining the SW-NIR spectra of fruit

B-coefficients of the sugars are very similar to those of intact apples, peaches and nectarines (Figure 4) in the 800–950 nm spectral region. This explains why these fruits exhibit excellent calibration and prediction results in the SW-NIR (for example, R^2 for apples (100 fruit, 10 PC), was 0.921, *SEC* = 0.227, *RMSECV* = 0.276, *SD* = 0.99).

Table 1. PLS1 calibration on sugar concentration (absorbance data, 700–1050 nm, temperature added as an *x* variable).

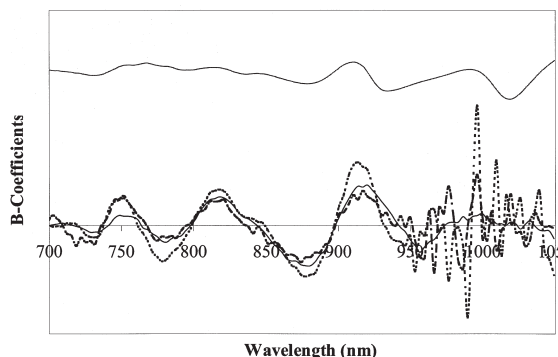| Sugars	#Samples	#PC	R^2	*SEC*	*RMSECV*	Mean	*SD*
Sucrose	429	4	0.993	1.10	1.12	26.48	13.50
D-Glucose	362	3	0.987	1.83	1.86	23.12	16.30
D-Fructos	359	4	0.993	1.29	1.32	23.09	16.30

Figure 4. Plot of regression coefficients from PLS calibration on °Brix for apples, peaches and nectarines (absorbance data, 700–1050 nm, temperature added as an *x* variable) (— apples, --- peaches, –·– nectarines). Curve on top represents regression coefficients from PLS calibration on concentration (% w/w) for sucrose solutions, obtained under the same conditions.

Acknowledgements

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