Investigating Aquaphotomics for Fruit Quality Assessment

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Summary: In our research work, we are investigating aquaphotomics with simple systems, such as sucrose solution of various concentrations, and an aqueous system such as kiwifruit juice, and finally on whole intact kiwifruit. Our analysis focuses on the first (1300-1600 nm) and second (800-1100 nm) overtone regions of water. The key question is: Can aquaphotomics help in developing better prediction models for intact fruit analysis? For a simple aqueous system, water bands were identified in first and second overtone regions that can explain water structure according to soluble solid content (SSC) concentration. We found that for generating meaningful aquagrams of aqueous samples in first and second overtone regions, sample path length plays an important role. The partial least square regression (PLSR) model built in the second overtone region with 10 mm path length gave a standard error of prediction (SEP) of 0.11% which was comparable to first overtone prediction results using a 1 mm cell. This confirms that longer path-lengths are essential for the short wavelength second overtone region and hence for solid samples such as kiwifruit, where light travels longer path lengths. The PLSR model built in the 800-1000 nm region (second overtone) gave better result with a SEP of 0.41 % compared to 0.64% in the 600-1100 nm range signifying that the important information resides in the tight window of the second overtone region.

Introduction:

Near infrared (NIR) spectroscopy is a fast, non-destructive, and non-invasive technique used to predict the quality parameters of fruits such as dry matter and SSC. Fruits like apples and kiwifruit are more than 80% water. The NIR spectrum of whole intact fruit is dominated by water absorption peaks that shift and vary in shape in accordance to changes in quantities such as sugar content [1]. These changes can significantly reduce the predictive model performance for quality parameters. Aquaphotomics is a branch of near infrared spectroscopy in which the spectral analysis focuses on absorbance patterns related to water bands and the effect of perturbations due to variation in temperature, concentration of solutes, environment, etc. [2]. As the water peak at 1450 nm (first overtone) and 970 nm (second overtone) in the samples varies due to SSC concentration, we have investigated the aquaphotomics approach to learn more about changes in the water structure that are apparent in the 1300-1600 nm and 800-1100 nm wavelength regions.

In the present study, we have identified water bands for SSC variation in the first and second overtone region for our samples. Models are built on aqueous samples using measurements from two transmission cuvettes of differing path lengths, set to optimize the signal to noise (SNR) for the first and second overtone region, respectively [3]. We have built calibration models for SSC prediction of kiwifruit juice at one temperature using measurements from an FT-NIR spectrophotometer. For intact whole fruit measurements, data was collected using a portable NIR spectrophotometer. Data modelling used PLSR and standard normal variate (SNV) pre-processing techniques.

Methods:

A total of 100 Gold Kiwifruit *"Actinidia chinensis"* were purchased from New Zealand retail stores. Non-destructive NIR measurements were made on intact fruit, then juice was extracted from squeezed endcaps. The juice was collected in Eppendorf tubes and was filtered through 0.2 µm filter paper to get clear juice. The samples were stored in a refrigerator at 4 °C. FT-NIR analysis and reference measurements were performed the next day after the samples were equilibrated to room temperature of 22 °C. For reference data, the SSC (%) of the kiwifruit juice samples was measured by a digital refractometer (Atago Co. Ltd, Tokyo, Japan).

Non-destructive NIR interactance measurements were acquired in the 300-1100 nm range using a handheld NIR instrument (F-750 Produce Quality Meter; Felix Instruments, Portland, USA). Fruit spectra were recorded taking two separate measurements on opposite sides in the equatorial plane of each fruit. Destructive transmittance spectra of the juice samples were measured at 22 °C (±1 °C) with a FT-NIR spectrometer (Tango, Bruker Corporation, Germany) equipped with a temperature-controlled holder. Two measurements were acquired for each juice sample using quartz cuvettes of 1 mm and 10 mm optical path length, respectively. For each measurement one spectrum, which was the average of 32 successive scans, was recorded for the range 870-2500 nm with a resolution of 16 cm^{-1}. Measurements with 1 mm and 10 mm path length cuvettes were also taken on Milli-Q water and sucrose solutions with SSC varying from 5 to 17.5 % with a step increase of 2.5 %.

Predictive models were developed using MATLAB version R2017a (Math Works Inc., Natick, USA) and the PLS toolbox version 8.1.1 (Eigenvector Research Inc., Wenatchee, USA) with four-fold venetian blind cross validation applied. The spectral data were pre-processed using SNV. Four samples were considered outliers (probably due to clerical blunders) and were removed from the dataset. The main data set was first rank ordered as per SSC value and then split by a 3:1 venetian blind method into a calibration (63 samples) and validation (33 samples) set (Table 1). The calibration models were developed using PLSR techniques for predicting SSC of juice and intact fruit samples.

Results and Discussion:

The aquagram in Fig.1 illustrates that, as the SSC level rises in kiwifruit juice, the number of strongly hydrogen-bonded water molecules (S3, S4: water molecules with three and four hydrogen-bonds, and (v1, v2): symmetrical stretching fundamental vibration) increases, resulting in highly organised water structures.

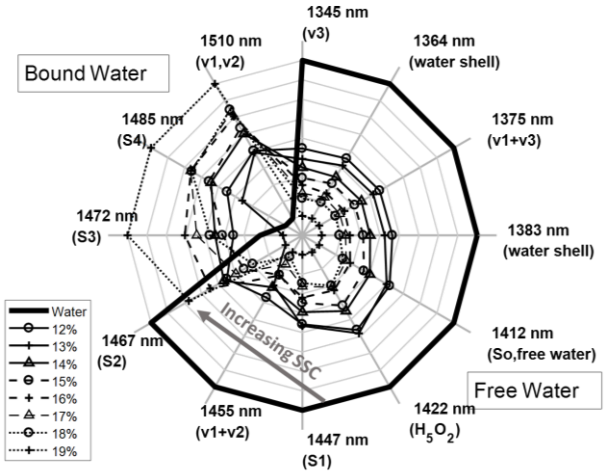

Fig. 1 Aquagram of kiwifruit juice samples showing an increase in bound water with SSC in the first overtone region.

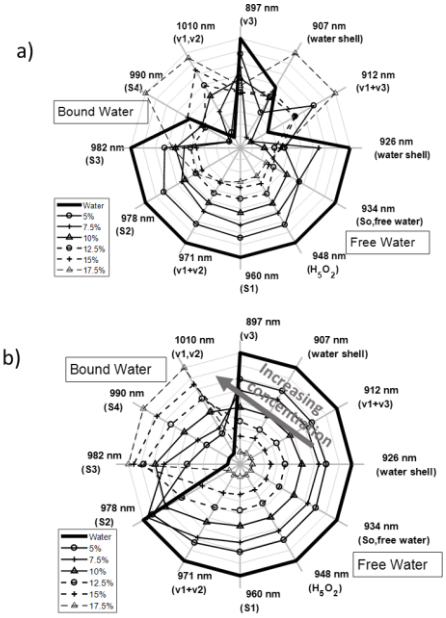

Fig. 2 Aquagram of sucrose solutions in the second overtone region using a) 1 mm path length cuvette and b) 10 mm path length cuvette.

The aquagrams of sucrose solutions in the second overtone region (870-1100 nm) are shown in Fig. 2(a) and 2(b), respectively. Using a longer pathlength cell of 10 mm for second overtone region measurements (Fig 2(b)), the ambiguity of the water spectral pattern (WASP) compared to the 1 mm pathlength cell (Fig. 2(a)) is reduced. Moreover, there is an improvement in model performance for SSC prediction of kiwifruit juice with a 68% reduction in standard error of prediction (SEP) when using the 10 mm path length cell measurements in the 870-1100 nm region (Table 1). Therefore, the path length of the sample cell is an important factor for improving aquaphotomics interpretation in short wave-NIRS since light has longer penetration depth in this region. For whole intact fruit, the PLRS model gives better results in the reduced 800-1000 nm region with SEP of 0.41% in comparison to 0.64% in 600-1100 nm region.

Table 1. Comparison of SSC prediction model performance for kiwifruit juice and for intact whole kiwifruit

PLS	(N_{cal}=63 and N_{val}=33)							
Pathlength/ Sample	**Wavelength range, nm**	**R^2_{cv}**	**RMSECV**	**LV**	**R^2_p**	**RMSEP**	**Bias**	**SEP**
1 mm (Juice, FT-NIR)	1300-1600	0.99	0.13(± 0.01)	7	0.99	0.13(± 0.03)	0.02	0.13
	870-1100	0.94	0.31(± 0.04)	7	0.93	0.37(± 0.09)	0.09	0.35
10 mm (Juice, FT-NIR)	870-1100	0.99	0.13(± 0.02)	7	0.99	0.11(± 0.02)	0.01	0.11
Intact whole fruit (F-750)	600-1100	0.75	0.70(± 0.02)	14	0.79	0.65(± 0.09)	0.08	0.64
	800-1000	0.88	0.47(± 0.03)	8	0.91	0.43(± 0.06)	0.12	0.41

N_{cal}/N_{val}: the number of samples in calibration/validation set; R^2_{cv}/R^2_p: the coefficient of determination for calibration/prediction; RMSECV/RMSEP: root mean square error of calibration/prediction; SEP: standard error of prediction (bias corrected RMSEP); LV: latent variable.

References:

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