

Assessment of Apple Juice by Aquaphotomics in a Temperature Dependent Environment

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Abstract: Aquaphotomics and extended multiplicative scatter correction (EMSC) combined with partial least squares regression (PLSR) of near infrared spectra were investigated to predict apple juice brix at different temperatures. Biases reduced to insignificant level.

OCIS codes: (300.0300) Spectroscopy; (120.6200) Spectrometers and spectroscopic instrumentation; (120.6780) Temperature; (010.7340) Water

1. Introduction

The near infrared (NIR) spectrum of water is sensitive to temperature variations [1, 2]. Since apple juice consists of more than 85% of water, its spectral signature is also affected by temperature perturbations. The shift in the spectrum can introduce a bias when developing calibration models from these spectra. Until now, researchers have studied the effect of temperature on prediction models of intact fruit dry matter (DM) [3]. Others have developed a calibration equation with temperature compensation for determining the brix value in intact peaches [4]. It was found that the calibration equation developed using samples at one fixed temperature could not reliably predict sample properties at a different temperature. A multivariate technique called EMSC has been used to remove the component affected by temperature ($\pm 1^\circ\text{C}$) from spectra of salt solutions [5].

As the water peak at 1450 nm in fruit juice samples shifts due to temperature variation, we have investigated a new approach called “Aquaphotomics” to learn more about changes in the water structure caused by the temperature perturbation in the 1300-1600 nm wavelength region. 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. [6]. In the present study, we have built calibration models for brix prediction of apple juice using a FT-NIR spectrophotometer and PLSR with EMSC correction.

2. Material and Methods

The juice from 120 Braeburn apples purchased from New Zealand retail stores was extracted by cutting them and squeezing the cut part of the fruit. Then, the juice samples were collected in 2 ml Eppendorf tubes. The samples were frozen and stored at -10°C until FT-NIR analysis and reference measurements were performed on the thawed samples. Before the brix measurement, the samples were centrifuged to get a clear solution. For reference measurement, the brix of the apple juice samples was measured by a digital refractometer (Atago Co. Ltd, Tokyo, Japan).

The transmittance spectra of the juice samples were measured at 20°C , 25°C , and 30°C ($\pm 1^\circ\text{C}$) with a FT-NIR spectrometer (Tango, Bruker Corporation, Germany) equipped with a temperature controlled holder fitted with a quartz cuvette (1 mm optical path length). Spectral acquisition was performed saving three consecutive spectra in the range of 870-2500 nm at 0.6 nm spectral step. All saved spectra were the average of 32 successive scans with a resolution of 16 cm^{-1} . The total number of juice spectra were 1080 (120 samples x 3 consecutive scans x 3 temperatures). In order to monitor any interfering signal, a control spectrum of Milli-Q water was taken after every eleventh apple juice measurement. Therefore, the total number of water spectra were 99 (11 samples x 3 consecutive scans x 3 temperatures). After omission of three samples because of clerical errors and six outliers, the final data set consisted of 111 apple juice samples (999 spectra). The spectral region above 1800 nm was discarded due to the high absorption in aqueous samples.

Predictive models were developed using MATLAB version R2014b (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 samples were rank ordered as per brix value. The spectral data were pre-processed using two techniques: Standard normal variate followed by a second derivative transformation (SNV+2D) and EMSC correction (equation 1). The main apple juice data set was split into three temperature subsets at 20°C , 25°C , and 30° and a calibration (83 samples) and validation (28 samples) set (Table 1). A calibration model was developed using the samples at 20°C that was later applied to samples at 20°C , 25°C and 30°C for brix prediction.

3. EMSC correction

The EMSC model can be described by the equation:

$$X = b_0 + b_1 \bar{X} + b_2 I + e \quad (1)$$

where X is the observed spectra at all three temperatures, b_0 , b_1 , and b_2 are constants, I is the interfering spectrum (*i.e.* the PC1 loading of water samples in our case), \bar{X} is the reference spectrum (the mean of spectra at the three temperatures) and e is the residual.

4. Results and Conclusion

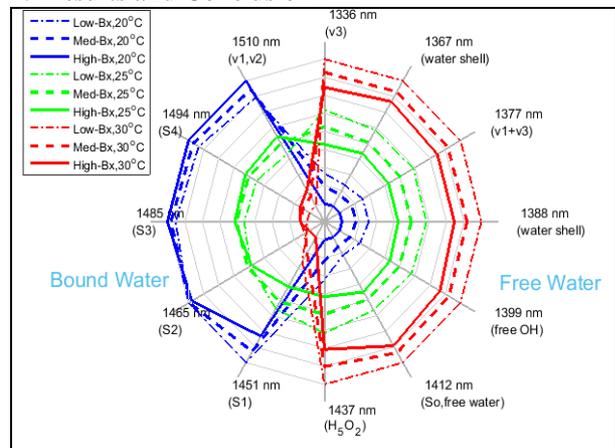


Fig. 1 Aquagram at three temperatures for low, medium and high brix level apple juice samples based on water matrix coordinates [6].

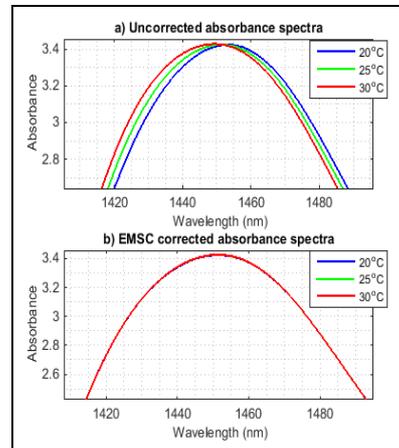


Fig. 2 Uncorrected (a) and EMSC corrected (b) apple juice spectra generated by removing PC1 loading component of water samples from apple juice spectra.

The aquagram in Fig.1 illustrates that free water (free OH and S_0 : water molecules with no hydrogen(H)-bonds) increases with temperature due to breaking of H-bonds. As the brix level rises, the number of strongly H-bonded water molecules (S_2 , S_3 , and S_4 : water molecules with two, three, and four H-bonds) increases resulting in highly organised water structures. The uncorrected absorbance spectra are shown in Fig. 2(a) and the EMSC corrected ones with the wavelength shifts removed in Fig 2(b). By using EMSC pre-processing, 79% and 93.5% reduction in bias were observed in comparison with SNV+2D pre-processing while predicting brix at 25 and 30°C with the model developed by samples at 20°C. Moreover, there was an improvement in model performance with 6-8% reduction in standard error of prediction (SEP) (Table 1).

Table 1. Comparison of SNV+2D and EMSC preprocessing method in 1300-1600 nm region

Cal = 20°C	(N _{cal} =83 and N _{val} =28)							
Val =	Pre-processing	R ² _{cv}	RMSECV	LV	R ² _p	RMSEP	Bias	SEP
20°C	SNV+2D	0.82	0.50(± 0.03)	2	0.81	0.52(± 0.11)	0.07	0.51
	EMSC	0.83	0.49(± 0.03)	1	0.83	0.49(± 0.09)	0.07	0.48
25°C	SNV+2D	0.82	0.50(± 0.03)	2	0.81	0.62(± 0.10)	0.29	0.51
	EMSC	0.83	0.49(± 0.03)	1	0.83	0.49(± 0.10)	0.06	0.48
30°C	SNV+2D	0.82	0.50(± 0.03)	2	0.77	1.01(± 0.25)	0.77	0.58
	EMSC	0.83	0.49(± 0.03)	1	0.79	0.54(± 0.11)	0.05	0.53

N_{cal}/N_{val}: the number of samples in calibration/validation set; R²_{cv}/R²_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.

5. References

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