

On-line versus at-line analysis of carbohydrates in fruit juice

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Introduction

Water is a strong absorber in the infrared part of the electromagnetic spectrum and near infrared (NIR) spectra of samples with high water contents (> 80%) are strongly dominated by the sample water. NIR technology was, therefore, for a long time, considered problematic for liquid samples. However, in recent years several NIR techniques for liquid samples have been reported.¹⁻⁴ These techniques can be divided into the following three groups:

1. off-line techniques: for example, transmittance measurements in cuvettes/sample cups and the dry extract spectroscopy by infrared reflectometry (DESIR) technique, both performed in the laboratory
2. at-line techniques: direct transmittance and transreflectance measurements with fibre optics, performed at the production line
3. on/in-line techniques: direct transmittance and transreflectance measurements with fibre optics, performed on or in the production line.

The advantages of on/in-line measurements are obvious, involving time, cost and effort savings. The typical disadvantage of the use of fibre optics is loss of precision. Improvements on equipment and in data processing methods can reduce this problem significantly. In this experiment, the levels of sucrose, fructose and glucose in fluid food systems with scatter (orange juice) and without scatter (water) have been studied using at-line transreflectance and on-line transmittance measurements.

Experimental

Samples

Samples of orange juice from the same batch were spiked with 0–1.6% sucrose (α -D-glucopyranosyl- β -D-fructofuranoside), fructose (β -D-fructofuranose) and glucose (α -D-glucopyranose), all from BDH Laboratory Supplies, Poole, UK. The mixtures were designed to contain a total of 2.4% of added carbohydrate, using nine levels with 0.2% steps for each carbohydrate, as illustrated in Figure 1. The original orange juice was analysed by HPAELC (high pH anion exchange liquid chromatography) at AnalyCen, Moss, Norway.

The non-scattering model system was designed in the same way as the scattering system, using distilled water as a solvent.

Spectra

The transreflectance and transmittance spectra were recorded using a Foss NIRSystems 6500 scanning spectrophotometer (400–2500 nm, 2 nm steps, 32 scans per sample) equipped with fibre optical probes and Vision® v. 2.00 software (all from Foss NIRSystems Inc., Silver Spring, MD, USA). The transreflectance spectra were obtained from the samples in aluminum covered plastic bottles during

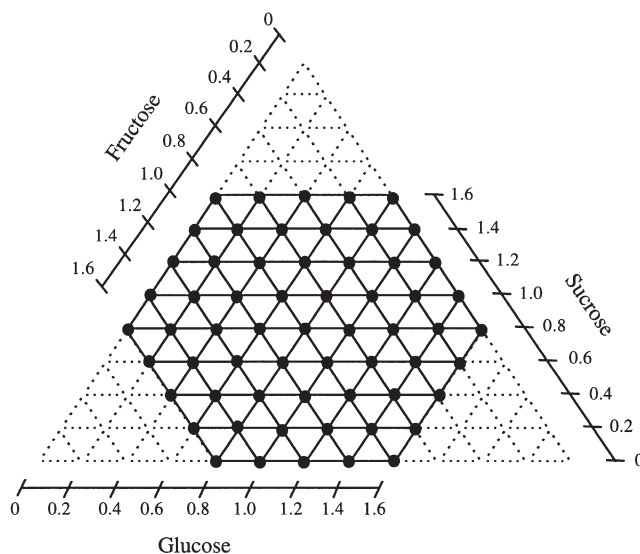


Figure 1. Simplex design with cut-off edges, containing samples with different levels of sucrose, fructose and glucose (%).

mixing by a magnetic stirrer. A diffuse mirror was used with the transmittance probe. The transmittance spectra were recorded in a closed loop flow system consisting of a peristaltic pump, plastic and glass tubes. The probes were mounted in an aluminum covered plastic cross-linkage. The laboratory experimental rig was constructed to simulate a production line. For both measurement techniques, spectra were recorded with 1 and 10 mm pathlengths (i.e. 5 mm between the end of the fibre bundle and the mirror for the transmittance probe), using air as reference. The linear flow speed of the fluid passing through the cross-linkage was found to be 0.33 ms^{-1} for 1 mm pathlengths and 0.03 ms^{-1} for 10 mm pathlengths. All samples were temperature-controlled during the measurements and spectra were recorded within limits of $22 \pm 0.5^\circ \text{C}$.

Data treatment

For all spectra, the wavelength regions below 780 nm and above 2350 nm were removed. Visual inspection of 25% fructose, glucose and sucrose spectra showed clear separation in the area 2100–2350 nm. Separations were also found in the areas 1100–1300 nm and 1500–1870 nm. High water absorbance gave saturation of the signals at the 1870–2100 band and this wavelength region was, therefore, deleted prior to calibration. For further data treatment MATLAB® version 4.2c.1 was used. The spectral regions studied were: 1) 780–1100 nm, 2) 1100–1300 nm, 3) 1100–1870 nm and 4) 2100–2350 nm. Partial least squares (PLS) regression⁵ was performed on the averaged $\log(I_0/I)$ triplicate spectra and the models were validated using full cross-validation.⁶ The following pre-processing methods were evaluated for calibrations prior to averaging: multiplicative scatter correction (MSC), 1st and 2nd derivatives, Savitzky–Golay smoothing and baseline corrections.

Results and discussion

The original orange juice was analysed to contain 4.6% sucrose, 3.2% fructose and 2.3% glucose. None of the pre-processing methods studied were found to significantly lower the prediction errors,

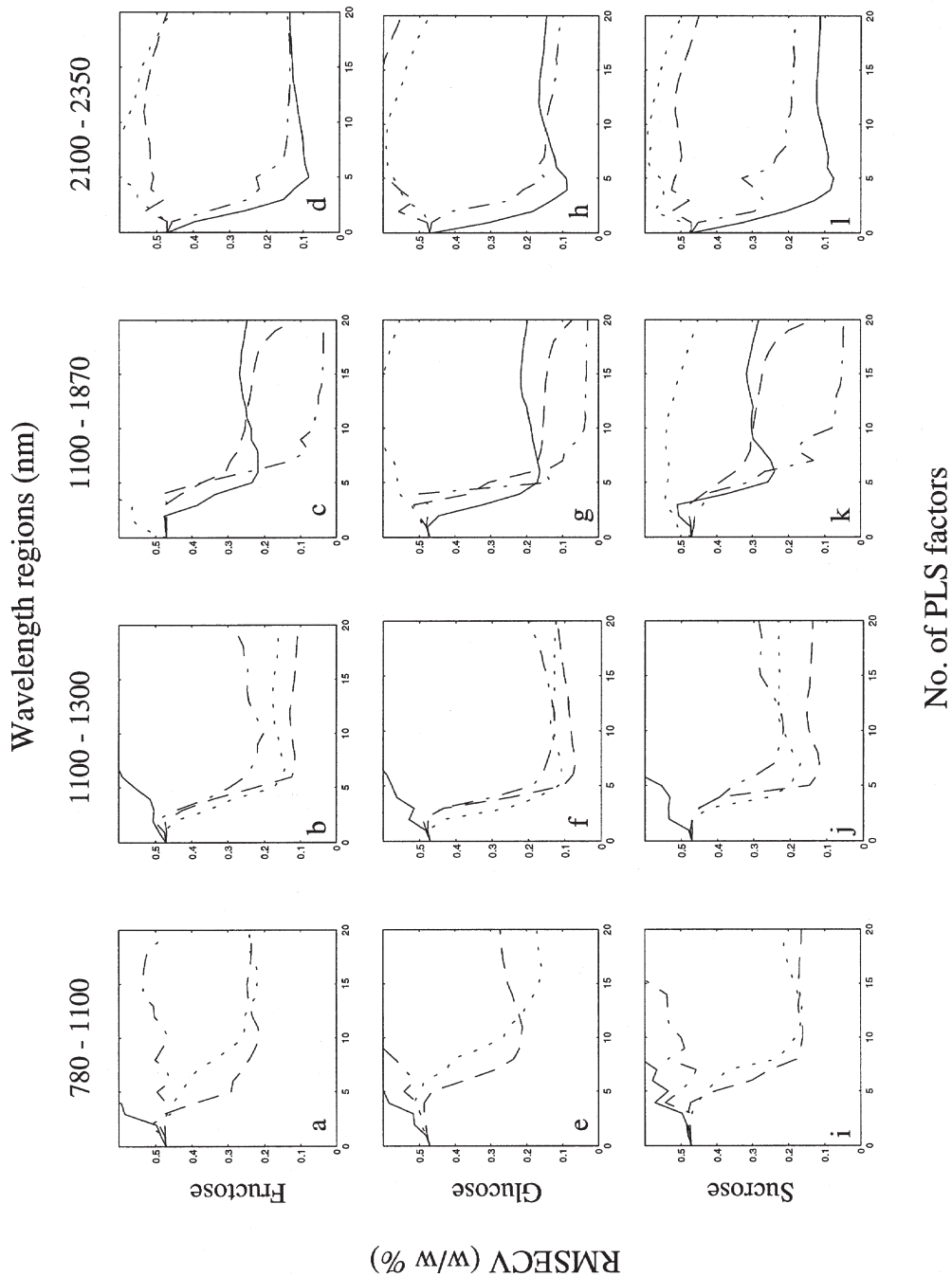


Figure 2. This figure illustrates *RMSECV* as a function of the number of PLS factors for prediction of carbohydrates in orange juice solutions. —: On-line 1 mm, ···: at-line 10 mm, - - - : at-line 10 mm and _ _ _ : at-line 10 mm.

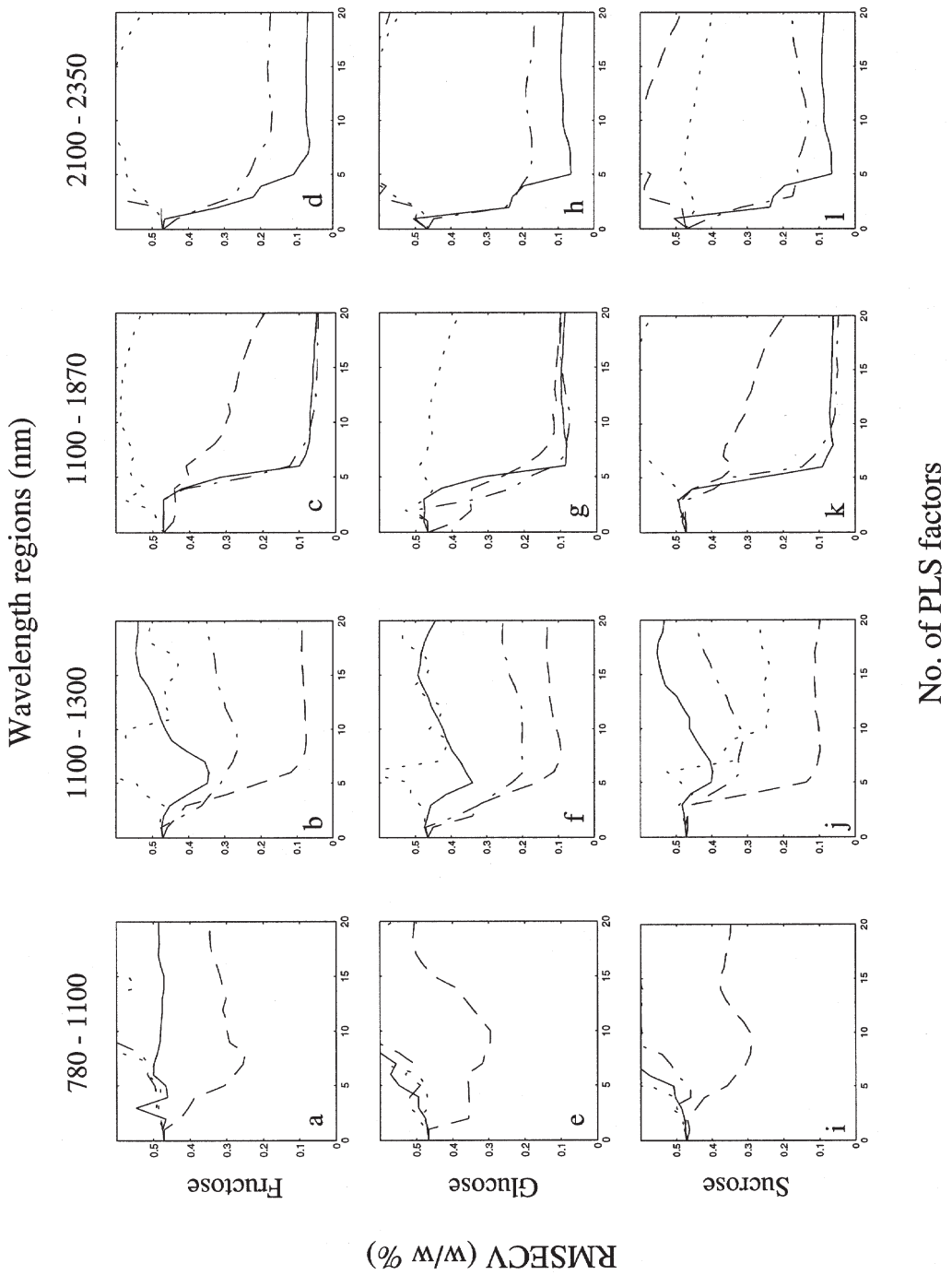


Figure 3. This figure illustrates *RMSECV* as a function of the number of PLS factors for prediction of carbohydrates in water solutions. _____: on-line 1 mm, - - - : at-line 10 mm,: on-line 10 mm and _____: at-line 10 mm.

neither for scattering nor for non-scattering media. All results are, therefore, based on models calculated from $\log(I_0/I)$ spectra.

Figures 2 and 3 illustrate the cross-validated root mean square error of prediction (*RMSECV*) as a function of the number of PLS factors for the three carbohydrates in each of the four investigated spectral regions, for orange juice and water samples, respectively. The figures illustrate that the 780–1100 nm area also gave poor prediction errors for the 10 mm measurements. The 1100–1300 nm region gave lower prediction errors for the 10 mm measurements than the 780–1100 nm region.

In the spectral region 1100–1870 nm, the scattering model system with at-line 1 mm measurements gave the lowest *RMSECV* (w / w%), with values of 0.0355, 0.0318 and 0.0482 for fructose, glucose and sucrose, respectively, using 20 PLS-factors (Figure 2). This result was far better than the on-line measurements in this spectral region. Also for the non-scattering model system (Figure 3), the lowest prediction errors were obtained in the 1100–1870 nm region, but here on-line and at-line measurements gave similar prediction error results. The on-line 1 mm measurements gave minimum *RMSECV* (w / w%) of 0.0533 (eight PLS-factors), 0.0826 (20 PLS-factors) and 0.0609 (eight PLS-factors) for fructose, glucose and sucrose, respectively.

In the upper region of the near infrared (2100–2350 nm), the on-line 1 mm measurements performed better than the at-line measurements. Visual inspection of the $\log(I_0/I)$ spectra indicated that the at-line spectra had higher absorbance levels than the on-line spectra and that the former showed tendencies of saturation and non-linearities.

The 10 mm on-line water measurements did not perform well in the calibrations and could not be used for comparable calibration models.

Conclusions

For the orange juice model system, at-line NIR measurements outperformed the on-line measurements. For the non-scattering model system, on-line and at-line measurements gave similar prediction error results. Models giving the lowest prediction errors for both measurement techniques were obtained in the 1100–1870 nm region, using 1 mm pathlengths. 10 mm pathlengths gave substantially higher prediction error results than 1 mm pathlength measurements.

References

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