Outer product analysis applied to time-resolved reflectance spectroscopy (TRS) and NIR reflectance spectra of apples

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Introduction

Time-resolved reflectance spectroscopy (TRS), differently from continuous-wave NIR methods, can separate the effects of light absorption (related to chemical composition, e.g. chlorophyll and water contents), and light scattering (related to structural properties), by measuring photon time-of-flight distribution with picosecond temporal resolution. By the application of TRS in measurement campaigns on fruits, it was found that absorption and scattering coefficients at selected wavelengths in the 600–1000 nm spectral range were related to some internal quality attributes and to fruit maturity in apples, pears and nectarines.[1–4] Although TRS and NIR share the same physical principles (i.e. light–matter interaction), a direct and systematic comparison of these two techniques has not been accomplished in apple fruit. The aim of this work was to compare the calibration performance for firmness, water content and soluble solid content in apples as obtained from TRS and NIR measurements, and to visualize the simultaneous variations of the NIR and TRS spectra associated with each parameter by Outer Product Analysis (OPA).

Materials and methods

One hundred and twenty apples (60 Pink Lady® and 60 Golden Delicious) were analysed by TRS and, after slicing, by NIRS. TRS measurements were carried out at 670 nm and in the range 740–1100 nm every 20 nm, with a broadband TRS system developed at Politecnico di Milano[5] on

two opposite sides of each fruit, and then averaged per fruit. The reduced scattering coefficients (μ'_s) and the absorption coefficients (μ_a) were obtained by fitting the experimental TRS data with a standard solution of the diffusion approximation to the transport equation for a semi-infinite homogenous medium. The extrapolated boundary condition was used[6] to take into account the refractive index mismatch at the surface. With such a system, the reproducibility error (CV over repeated measurements on different days) was less than 4% for both μ_a and μ'_s at each wavelength. More details of the procedures for estimating absorption and scattering coefficients from TRS data can be found in Cubeddu *et al*.[7] NIRS measurements were performed using a FT-NIR (NIRFlex N500, Büchi, Italy) equipped with a fibre probe. On three slices/fruit, spectra were collected twice over the NIR range from 1000 nm to 2500 nm. The NIR averaged spectra were pretreated with the EMSC algorithm. Calibration models for water content, soluble solid content (SSC) and firmness, estimated by standard destructive techniques, were calculated using the PLS_Toolbox (Eigenvector Research, Inc., USA); OPA was carried out using a software package developed by Barros[8] and Barros *et al*.[9] applying partial least squares (PLS) regression to the OP matrix.

Results and discussion

In Figure 1 are shown both the absorption (μ_a, cm^{-1}) (a) and the reduced scattering coefficients (μ_s', cm^{-1}) (b) for all the apple fruit.

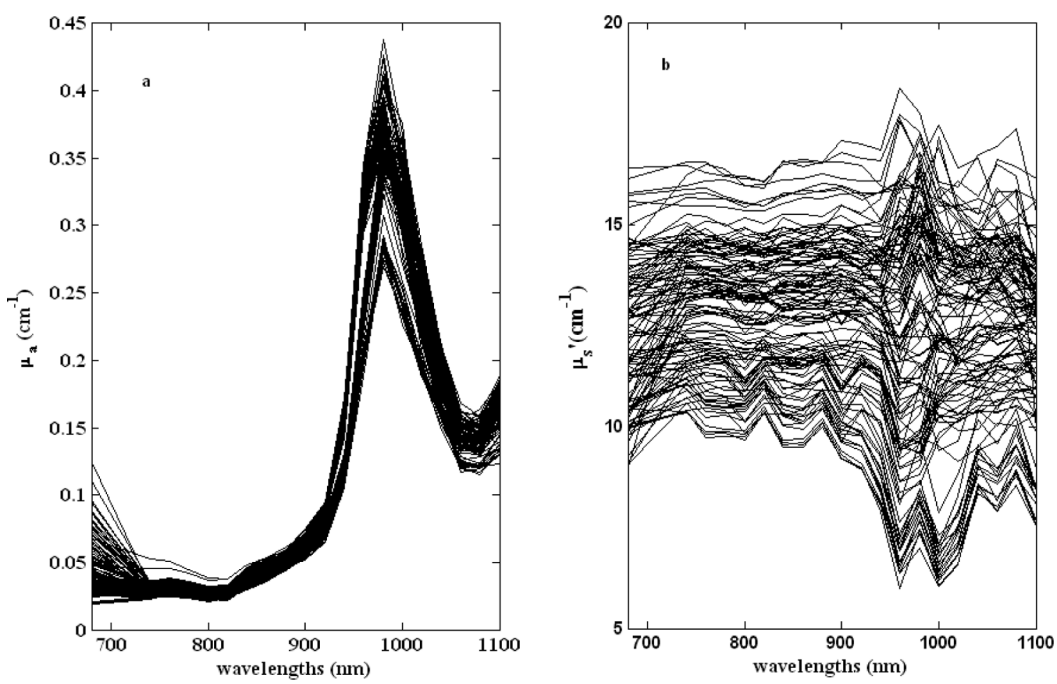

Figure 1. Spectra of absorption (μ_a, cm^{-1}) (a) and the reduced scattering coefficients (μ_s', cm^{-1}) (b) measured by TRS (each line corresponds to one fruit).

Table 1. Calibrations performances for firmness, water and SSC content in apples.

	Parameters		Regression results								
			NIR			TRS (absorption)			TRS (scattering)		
	Range	SD	LV	R^2 prediction	RMSECV	LV	R^2 prediction	RMSECV	LV	R^2 prediction	RMSECV
	Pink Lady® apples										
Firmness (N)	37.40 ÷ 99.40	16.64	10	0.865	9.88	11	0.886	7.44	4	0.650	9.80
Water content (%)	83.10 ÷ 85.50	0.56	8	0.791	0.30	3	0.449	0.44	3	0.017	0.57
SSC (°Bx)	12.90 ÷ 15.26	0.49	10	0.820	0.33	4	0.433	0.37	3	0.410	0.44
	Golden Delicious apples										
Firmness (N)	32.60 ÷ 78.60	11.73	10	0.782	5.6	3	0.744	5.60	4	0.822	4.67
Water content (%)	81.81 ÷ 86.61	1.04	12	0.848	0.40	3	0.204	0.71	3	0.426	0.77
SSC (°Bx)	12.42 ÷ 16.32	0.93	8	0.823	0.39	5	0.297	0.75	3	0.413	0.71
	Whole apple set										
Firmness (N)	32.60 ÷ 99.40	16.41	11	0.803	7.11	13	0.807	7.17	9	0.755	8.54
Water content (%)	81.81 ÷ 86.53	0.68	12	0.746	0.42	10	0.160	0.66	3	0.229	0.61
SSC (°Bx)	12.42 ÷ 15.38	0.65	11	0.789	0.35	10	0.316	0.56	3	0.324	0.55

In the absorption spectra there are two maxima: at 670 nm, corresponding to the absorption peak of chlorophyll-a, and at 980 nm, related to water. As for μ_s' spectra, there were some problems of crosstalk between absorption and scattering over the range 900–1000 nm resulting in a worsening of the estimation of μ_s' so these coefficients weren't taken into account.

Considering Pink Lady® apples (Table 1), better regression models were obtained for firmness with TRS absorption, whereas the firmness of Golden Delicious fruit was better predicted with TRS reduced scattering coefficients.

Generally NIRS gave better calibration models for the prediction of water content and SSC. TRS couldn't predict these two properties satisfactorily as can be seen by the low performances of regressions obtained: the coefficients of determination for prediction weren't higher than 0.45. The OPA results provided some information about the relationships between NIR and TRS: the principal NIRS absorptions involved in these relationships are related to the presence of water and sugar.

In Figure 2, representing the Pink Lady 2D plot of B-coefficients obtained by PLS regression between NIR-TRS absorption coefficients Outer Product matrix and SSC, a positive correlation was found between the NIR water combination band (1930 nm) and the TRS absorption coefficient at 980 nm (water).

There was a negative correlation among 1410 nm, 1820 nm and 2230 nm (sugar) NIR absorption and 960 nm and 1000 nm TRS absorption coefficients.

By contrast, the same NIR sugar absorption bands had a positive correlation with the 740 nm, 800 nm and 840 nm (water) reduced scattering coefficient, considering the relationships NIR-TRS obtained by PLS Outer Product matrix and firmness (Figure 3).

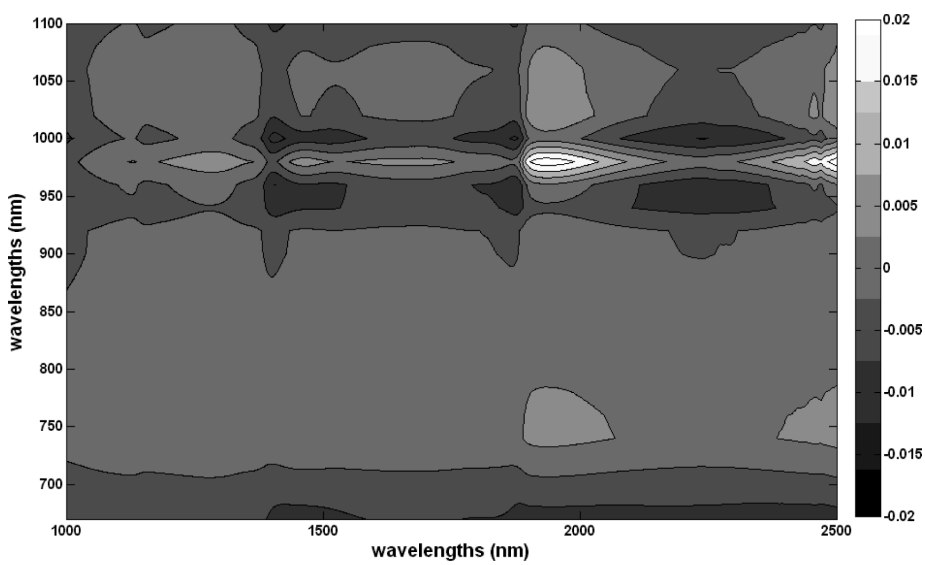

Figure 2. Pink Lady 2D plot of B-coefficients obtained by PLS regression between NIR-TRS absorption Outer Product matrix and SSC.

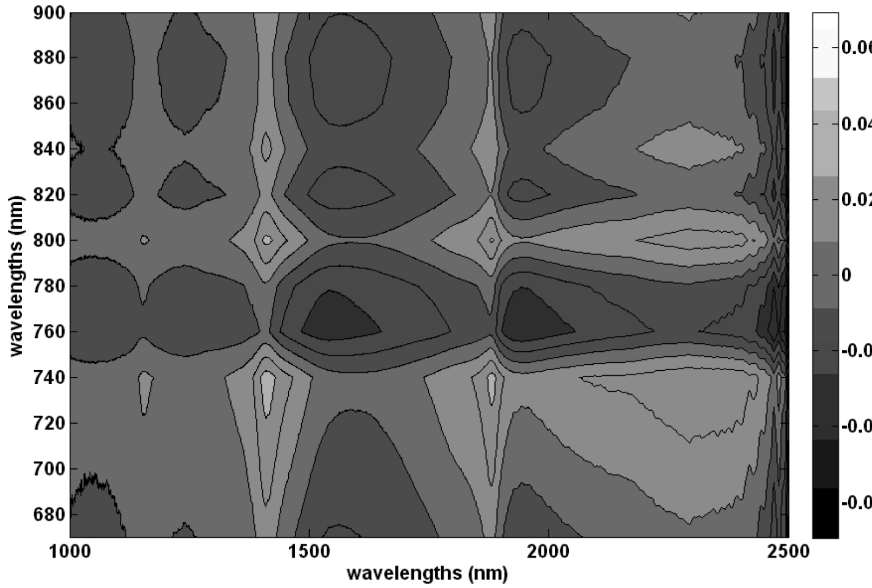

Figure 3. Golden Delicious 2D plot of B-coefficients obtained by PLS regression between NIR-TRS scattering Outer Product matrix and Firmness.

Conclusion

This preliminary study gave some useful information about the performance of TRS technique in predicting apple firmness. Ongoing analyses are already underway on this year's apple harvest, in order to confirm the use of TRS technique, and to investigate further relationships between the two different spectroscopy systems, NIRS and TRS.

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