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Research Paper

Non-destructive assessment of kiwifruit physico-chemical parameters to optimise the osmotic dehydration process: A study on FT-NIR spectroscopy

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ABSTRACT: Non-destructive rapid method based on FT-NIR spectroscopy is assessed to predict the processing response of raw materials at different ripening stages. During osmotic dehy-dration (61.5% sucrose solution, 5 h) ripe and unripe kiwifruits were analysed with FT-NIR spectroscopy and the most representative physico-chemical parameters to osmotic dehydration (dry matter, soluble solids content, water self-diffusion coefficient and firm-ness) were assessed by destructive measurements. Predictive models were successfully built by means of partial least square regression (PLSR) analysis ($R^2 > 0.772$, test set vali-dations) for all the four parameters destructively measured. The application of vector normalisation pre-processing was critical to eliminate spectral information that did not relate to the OD process. FT-NIR spectroscopy can successfully predict the evolution of kiwifruit physico-chemical parameters during osmotic dehydration. Thus it can be used as a tool to tune online the process parameters (e.g. time and temperature) to obtain a standardised final product starting from non-homogeneous raw materials.

Key words:
Ripening level
NIR spectroscopy
Kiwifruit
Osmotic dehydration
Non-destructive techniques

1. Introduction

Kiwifruit is one of the most suitable fruits to be osmo-dehydrated because its response to the treatment makes it possible to process raw unripe fruits, improving at the same time their firmness and taste (Bressa, Dalla Rosa, & Mastrocola, 1997).

Since the principal function of osmotic dehydration (OD) is tissue dewatering (Chiralt & Fito, 2003), it is important to study

and understand its effect on the water state and distribution inside the single cells, as well as in the whole cellular tissue. It is well known that OD promotes water activity reduction (Gianotti, Sacchetti, Guerzoni, & Dalla Rosa, 2001; Silva, Fernandes, & Mauro, 2014) and thus the decrease in freez-able water content (Cheng, Zhang, Adhikari, & Islam, 2014; Cornillon, 2000; Tylewicz et al., 2011), that makes it a suit-able process for the production of safe products with inter-mediate water content. However these parameters provide only general information about water in whole samples, in particular the water-solid exchange between the tissue and osmotic medium, without taking into account the water distribution in the different cellular compartments. Time domain nuclear magnetic resonance (TD-NMR) has been found to make up for these deficiencies, giving more detailed information about intensity and relaxation time (T_2) of protons separately for vacuoles, cytoplasm/extracellular spaces and cell wall (Cheng et al., 2014; Marigheto, Venturi, & Hills, 2008; Tylewicz et al., 2011). The OD process causes shrinkage of the vacuole and filling of intracellular spaces with external solution and vacuole content. These phenomena can be translated into the reduction of T_2 in both vacuole and cytoplasm/extracellular spaces compartments, while the intensity of the proton pool located in vacuoles and cytoplasm/extracellular spaces decrease and increase respectively (Panarese et al., 2012; Tylewicz et al., 2011). Recently Santagapita et al. (2013) used TD-NMR techniques to evaluate the water self-diffusion coefficient (D_w) both for whole kiwifruit tissue pro-tons and for each cellular compartment protons. The water self-diffusion coefficient depended on the distinctive cellular structures and solutes in kiwifruit and it decreased during OD due to water loss and sugar gain phenomena. Unfortunately NMR is a destructive method regarding the sampling procedure, since it involves cutting the sample into small cylinders of 7–8 mm of diameter. Moreover, difficulty and high cost of its application has forced researchers and industry to find other techniques, which could be non-destructive and with lower cost and higher availability. Near infrared (NIR) spectroscopy could be a good alternative for studying not only the basic information such as moisture and soluble solids contents but also diffusive phenomena. In order to study the latter, the correlation NIR/NMR response is necessary. Besides, several acquisition accessories are available for NIR spectroscopy, allowing the direct measurement of a desired product, leaving the sample unaffected.

NIR spectroscopy covers the wavelength range from 780 to 2500 nm. When the NIR radiation hits the product, the spectral characteristics change through wavelength dependent scat-tering and absorption. This change depends on the chemical composition of the product, as well as on its light scattering properties, which are related to the microstructure (Nicolaï et al., 2007).

In the past few years, NIR spectroscopy has been used to determine some physico-chemical parameters such as dry matter (or moisture content) and soluble solid content of several fruits. Particularly, dry matter (Qiang, Mingjie, Jianrong, Huazhu, & Chaitep, 2010; Slaughter & Crisosto, 1998), solid soluble content (Arazuri, Jarén, & Arana, 2005; Chen & Han, 2012; Slaughter & Crisosto, 1998), fructose, glucose and starch contents (Slaughter & Crisosto, 1998), acidity (pH) (Moghimi, Aghkhani, Sazgarnia, & Sarmad, 2010) and firmness (Liu, Guo, & Yue, 2011) have already been successfully predicted by NIR spectroscopy in ripe kiwifruit. Recently, the internal quality of Hayward kiwifruit has been assessed by a non-destructive method such waveguide spectroscopy (Ragni, Cevoli, Berardinelli, & Silaghi, 2012), in which the soluble solid content (SSC) and the Magness–Taylor flesh firmness were adequately predicted.

It is known that OD promotes critical changes in kiwifruit, regarding texture profiles, dry matter and SSC (Panarese et al., 2012; Santagapita et al., 2013). The magnitude of those changes depends on the maturity degree of raw kiwifruits and on the OD process. Thus, if the ripening state of different batches subjected to OD is different, the final product quality will be affected.

The aim of present work was to evaluate the feasibility of a non-destructive and rapid method based on NIR spectroscopy to determine the changes promoted by OD on kiwifruit at different ripening stages. This study could represent a very important tool to make rapid decisions about the optimum OD time, according to the desired product target.

2. Materials and methods

2.1. Raw materials

Kiwifruits (*Actinidia deliciosa* var *deliciosa* cv Hayward) with homogeneous size and refractometric index of 6.9 ± 0.8 °Brix were bought on the local market (a special unripe batch of kiwifruits was requested). Kiwifruits were sorted to eliminate damaged or defective fruit and were partially ripened at 4 ± 1 °C and 90–95% relative humidity (RH) in air. During storage, fruits with refractometric index values of 9 ± 1 and 14.1 ± 0.9 °Brix were selected and defined respectively as LB (low °Brix) and HB (high °Brix) kiwifruits.

2.2. Osmotic dehydration treatment

The kiwifruits were sliced (10 mm thick) transversally to their axis, removing the peel using a scalpel. Three slices from the central part of each kiwifruit were prepared, placed in mesh baskets and immersed in 61.5% (w/v) sucrose solution equilibrated at 25 °C. The OD solution concentration was chosen based on previous studies (Panarese et al., 2012; Santagapita et al., 2013; Tylewicz et al., 2011). The baskets (13 × 3 cm, diameter × height) were continuously stirred with a propeller. The rotational speed (0.2 g-force) was experimentally determined to assure negligible external resistance to mass transfer. Both LB and HB kiwifruits were subjected to OD for pre-established contact period of 0, 30, 60, 180, and 300 min. For each time–temperature condition 30 kiwifruit slices were processed, processing 300 kiwifruit slices in total. The product/solution ratio was about 1:4 (w/w) to avoid changes in the solution concentration during the treatment (Kowalska & Lenart, 2001; Singh, Bawa, & Ahmed, 1998). The temperature and stirring of the solution was maintained constant as reported by Tylewicz et al. (2011). After the OD process, the slices were removed from the osmotic solution, their surface rinsed with distilled water and gently blotted with tissue paper.

2.3. Non-destructive analysis: spectra acquisition by NIR spectroscopy

The diffuse reflectance measurements were carried out in a FT-NIR spectrometer, MATRIX-F (Bruker Optik GmbH, Ettlingen, Germany) using a 10 mm outer diameter head fibre-optic sampling probe (IN 261, Bruker Optik GmbH) equipped with a bifurcated fibre bundle to both illuminate the sample and collect the diffusely scattered light.

The spectra were collected directly on each slice, without any modification of the sample such as cutting. For each slice an averaged diffuse reflectance spectrum was collected. A first spectrum was obtained by placing the probe parallel to the slice central axis, in direct contact with the kiwifruit. The slice was then rotated 180° perpendicularly to its central axis and a second spectrum was collected. The two spectra were then averaged to minimise any possible effect due to the heterogeneity of the outer pericarp tissue. Each spectrum was recorded as log (1/R), where R is the relative reflectance, by averaging 32 scans. Spectral data were acquired at room temperature (21 ± 1 °C) from 4000 to 12,000 cm^{-1} with 8 cm^{-1} of resolution. The spectrometer was equipped with a quartz beam-splitter and a thermoelectrically cooled Indium–Gallium-Arsenide (TE-InGaAs) photodetector. The acquisition was performed in a double sided mode (forward-backward) and the interferogram size consisted of 7108 points. FT was conducted with phase resolution of 32 with Mertz phase correction mode, Blackman-Harris 3-term apodization function and zero-filling factor of 2.

2.4. Destructive analysis

2.4.1. Moisture content and soluble solids content

Kiwifruit slices were weighed before and after osmotic dehydration process. The moisture content of kiwifruit samples was determined gravimetrically from the difference in mass before and after drying in a vacuum oven (pressure $\leq$ 100 mmHg) at 70 °C. The drying was performed until a constant mass was achieved (AOAC 920.15, 2002).

Soluble solids content was determined at 20 °C by measuring the refractive index with a digital refractometer (PR1, Atago, Japan) calibrated with distilled water. Both the moisture and the soluble solids content determinations were performed in triplicate for each treatment condition.

2.4.2. Time domain nuclear magnetic resonance (TD-NMR) measurements: water self-diffusion coefficient

Cylinders of about 500 mg of kiwifruit outer pericarp tissue were cut with a core borer at about 2 mm distance from the slice surface and placed inside 10 mm outer diameter tubes so that they were within the active region of the radio frequency coil. The samples were analysed at 24 °C using a Bruker Minispec PC/20 spectrometer (Bruker Biospin Gmbh, Rheinstetten, Germany) with a 0.47 T magnetic field operating at a resonance frequency of 20 MHz.

Water self-diffusion coefficient (D_w) was determined with a pulsed field gradient spin-echo (PGSE) sequence (Stejskal & Tanner, 1965), consisting of a spin-echo pulse sequence where two controlled magnetic field gradients are applied respectively between 90° and 180° pulses and between the 180° pulse and the acquisition.

The accuracy of the applied gradient (G) values was assured by means of a calibration in the range 1.2–2.2 T m^{-1} using 1.25 g L^{-1} of $CuSO_4 \cdot 5H_2O$ water solution characterised by a known D_w value.

Single component analysis was applied as reported by Santagapita et al. (2013), since the water distribution of the kiwifruit outer pericarp tissue was considered homogeneous and thus characterised by a single self-diffusion coefficient.

2.4.3. Texture analysis

Puncture test was performed on the outer pericarp of kiwifruit slices using a TA-HDi500 texture analyser (Stable Micro Systems, Surrey, UK) with 5 kg load cell, equipped with a metal cylindrical probe of 6 mm diameter. The rate and the depth of penetration were 1 mm s^{-1} and 6 mm respectively (Beirão da Costa, Steiner, Correia, Empis, & Moldão Martins, 2006). Firmness (N) was evaluated as the maximum peak force value (Valdez-Fragoso, Soto-Caballero, Blanda, Welti-Chanes, & Mújica Paz, 2009). Two measurements for each kiwifruit slice were averaged (n = 30 for each OD condition).

2.5. Statistical analysis

Significance of the osmotic dehydration effects on moisture, soluble solids content, water loss, water-diffusion coefficient and firmness was evaluated by means of one-way analysis of variance (ANOVA, 95% significance level) using the software STATISTICA 6.0 (Statsoft Inc., Tulsa, OK, USA).

2.6. Chemometric analysis

Chemometric analyses were conducted using The Unscrambler v9.7 software (Camo Software AS, Oslo, Norway).

2.6.1. Pre-processing and principal component analysis Vector normalisation (VN), multiplicative scatter correction (MSC) and second derivative were used as pre-processing methods. These pre-processing methods have been success-fully applied in similar data obtained for kiwifruit (Chen & Han, 2012; Moghimi et al., 2010). The data were smoothed using Savitsky-Golay method (101 and 35 points for 5990–4250 and 9850–7960 cm^{-1}, respectively) prior to pre-processing to reduce the noise produced during acquisition. Principal component analysis (PCA) was conducted on diffuse reflectance data (n = 300). Through PCA, besides the reduction of the dimension of the variables, the effect on the variance contribution of wavelength (x-variables) and the different data pre-processing methods were assessed. Calibration was performed on n = 210 samples. A randomisation t-test of validation was used to compare the predictive accuracy of the model, by using 30% of the dataset (90 spectra randomly selected).

2.6.2. Prediction by partial least squares regression Prediction models for moisture, soluble solids content, water self-diffusion coefficient and firmness in HB and LB osmodehydrated kiwifruits were developed using partial least squares regressions (PLS). This procedure has been

successfully applied for different fruits for the non-destructive assessment of SSC (Arazuri et al., 2005; Chen & Han, 2012; Slaughter & Crisosto, 1998), DM (Qiang et al., 2010; Slaughter & Crisosto, 1998) and firmness (Liu et al., 2011), among other parameters. Individual PLS regressions (PLS1) were conducted by using the spectral acquisitions corresponding to the whole range of wavelengths and the data pre-processing method selected with reference to the results of the PCA. The process of extracting the optimal number of latent variables (LVs), important to avoid over-fitting and under-fitting, was determined by using the minimum value of predicted residual error sum of squares (PRESS). The prediction ability of a model is given as root mean square error of calibration (RMSEC) or prediction (RMSEP) and the correlation coefficient (r) between the predicted and measured value of the attribute. Calibration was performed by using the 70% of the dataset (210 spectra randomly selected), while the randomisation t-test of validation was used to compare the predictive accuracy of models, by using the 30% of the dataset (90 spectra randomly selected). The values of PRESS, RMSEC and RMSEP were calculated using the equations from the literature (Chen & Han, 2012; Liu et al., 2014; Qiang et al., 2010). Only three samples were excluded as outliers for all the predictions, considering their high leverage and high residual X-variance. The accuracy of the predictive model was also studied by calculating the residual predictive deviation (RPD) obtained by dividing the standard deviation (SD) of the reference values by the SEC (square error of calibration) (Williams & Norris, 2001).

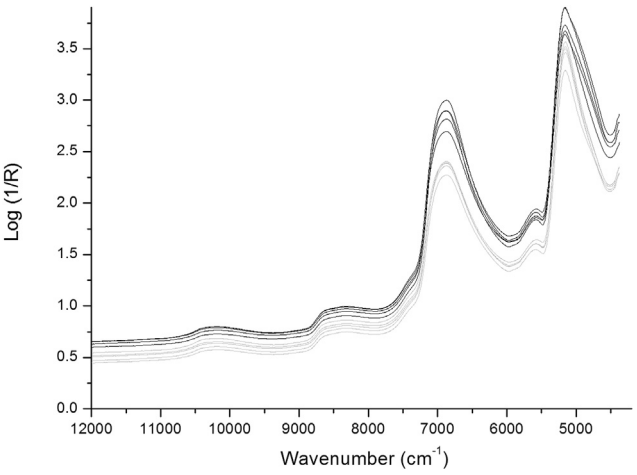

Fig. 1 – Average NIR spectra of low (grey lines) and high (black lines) °Brix kiwifruit groups osmo-dehydrated for different times (0–300 min). Each line corresponds to 30 kiwifruit samples.

3. Results and discussion

3.1. Mass transfer, water self-diffusion and textural results

Kiwifruit subjected to OD showed changes in their physico-chemical properties (Table 1). The OD treatment led both to an increase of soluble solids content and dry matter of the fruits and to a decrease of water self-diffusion coefficient (D_w) and firmness, showing similar trends for both kiwifruit groups.

The relationship between physico-chemical changes occurring during OD and the kiwifruit ripening stage have been further analysed and discussed in Panarese et al. (2012) and Santagapita et al. (2013). Schematically, these changes are the direct consequence of: i) water loss from the tissue caused by the difference in chemical potential of water between the product and osmotic medium (driving force); ii) gain of solutes present in osmotic medium by the tissue; iii) loss of cell membrane selectivity; iv) structural changes caused by the loss of cell wall integrity, loss of the cell turgor and plasmolysis, cell disruption, etc.

3.2. NIR prediction of physico-chemical changes promoted by osmotic dehydration (OD)

3.2.1. Effect of pre-processing and principal component analysis

Figure 1 shows the averaged NIR spectra of low and high °Brix kiwifruit groups osmo-dehydrated for different times (0–300 min). Kiwifruit NIR spectra can be influenced by the differences in chemical composition of the sample, the water content (since water is a strong NIR absorbent), and also, at a macroscopic level, by mechanical changes in kiwifruit hardness (Williams & Norris, 2001), which changes during OD, as shown by the firmness results reported in Table 1. Besides, NIR spectra are influenced by the multiple scattering due to

Table 1 – Soluble solids content (SSC), dry matter (expressed in dry basis, d.b.), water self-diffusion coefficient (D_w), and firmness (F) values of raw (0 min) and OD treated low and high °Brix kiwifruits. Average and standard deviation values are reported.

OD time	Low °Brix				High °Brix			
	SSC (°Brix)	Dry matter (% w $w_{d.b.}^{-1}$)	D_w (10^{-9} m^2 s^{-1})	F (N)	SSC (°Brix)	Dry matter (% w $w_{d.b.}^{-1}$)	D_w (10^{-9} m^2 s^{-1})	F (N)
0	9 ± 1^{e}	15.8 ± 0.7^{e}	1.66 ± 0.05^{a}	124 ± 19^{a}	14.2 ± 0.9^{e}	16.7 ± 0.8^{e}	1.51 ± 0.05^{a}	26 ± 6^{a}
30	11 ± 1^{d}	17.8 ± 0.9^{d}	1.58 ± 0.05^{b}	109 ± 19^{b}	16 ± 1^{d}	18.4 ± 0.8^{d}	1.47 ± 0.04^{b}	23 ± 4^{b}
60	13 ± 1^{c}	18.6 ± 0.9^{c}	1.60 ± 0.04^{b}	94 ± 13^{c}	17 ± 1^{c}	20 ± 1^{c}	1.42 ± 0.05^{c}	18 ± 5^{c}
180	16 ± 1^{b}	22.0 ± 0.9^{b}	1.49 ± 0.05^{c}	72 ± 12^{d}	20.3 ± 0.9^{b}	22.8 ± 0.7^{b}	1.34 ± 0.04^{d}	12 ± 3^{d}
300	19 ± 1^{a}	26 ± 1^{a}	1.43 ± 0.06^{d}	69 ± 14^{d}	23 ± 1^{a}	25.9 ± 0.8^{a}	1.23 ± 0.05^{e}	12 ± 2^{d}

Different letters in each column indicate significant differences ($p < 0.05$) on each parameter.

differences in contact between sample and NIR probe, as well as undesired scatter (baseline shifts and non-linearities) due to the comparable size of the NIR wavelength and particle size of the biological samples (like fruits) (Rinnan, van den Berg, & Balling Engelsen, 2009). These spectral differences should be removed as they are not informative about the changes promoted by OD, which could mean that the analysis of the unprocessed NIR spectra of Fig. 1 could lead to wrong interpretation of the data, since the true differences between spectra at different osmo-dehydration times are hidden. Thus, spectra pre-processing techniques were applied to the raw data. Three of the most common pre-processing methods (Rinnan et al., 2009) already used for NIR-kiwifruit spectra (Moghimi et al., 2010) were applied in the present work. The effect of the pre-processing methods on explained variance and number of principal components (PCs) is shown in Table 2. The vector normalisation (VN) method was selected as providing the highest explained variance with the lowest number of PCs. The MSC method gave very good results as well, by explaining more than 98% of the variance with four PCs, while the 2nd derivative method required two more PCs ($n = 6$) for the explanation of 94% of the variance, much poorer than the other two pre-processing methods.

The spectra obtained after VN processing (Fig. 2a) show a narrower absorption range than the spectra of Fig. 1, and now the differences along the spectra can be considered mainly related to the influence of water and sugar changes provoked by OD on kiwifruit slices. Figure 2b shows the score plot between PC1 and PC2, and the arrangement of the samples within and between the two kiwifruit groups (LB and HB). Figure 2b does not highlight clear or separate sub-groups, even though samples of the same OD time-ripening stage are located in the same region. This fact suggests that it would be better to define a single model for the prediction of each relevant parameter for the dataset containing both kiwifruit groups, instead of applying a model for each kiwifruit group. The X-loadings corresponding to the first two PCs (Fig. 2c), revealed that the X-variables (wavenumbers) between 5000 and 5500 and around 6900 cm^{-1} are the ones with highest contribution to the variance obtained for the measurements of LB and HB kiwifruits at different OD time. These wavenumbers correspond to the contributions of the first and the second overtones of water (with maxima around 6850 and 5180 cm^{-1}) and of sugars, particularly sucrose (with maxima around 6940 and 4807 cm^{-1}) (Williams & Norris, 2001), the two main chemical species affected by OD (Santagapita et al., 2013). The changes of these wavenumbers have already been considered for NIRS prediction in ripe kiwifruit of some physico-chemical parameters such as dry matter (Qiang et al., 2010; Slaughter & Crisosto, 1998), soluble solid content (Arazuri et al., 2005; Chen & Han, 2012; Slaughter & Crisosto, 1998), fructose, glucose and starch content (Slaughter & Crisosto, 1998) and firmness (Liu et al., 2011).

3.2.2. *Prediction of physico-chemical parameters*

The prediction of the physico-chemical parameters measured through destructive determinations was performed by using partial least squares regressions (PLSR) in which each dependent variable (dry matter, soluble solids content, water self-diffusion coefficient and firmness) was predicted from a large dataset of independent variables (1959 wavelengths). The parameters of the PLSR model are reported in Table 3. All PLSR were conducted with a validation set including 30% of the raw dataset.

Figure 3 shows the measured *vs.* predicted values for each variable obtained by PLSR for the four predicted parameters. All PLSR models performed for both kiwifruit groups employed between 9 and 12 latent variables (LV) in order to estimate each parameter. The estimation of the adequate number of latent variables is shown in Fig. S1 of Supplementary File (available online). The number of latent variables was selected as the first minimum of the PRESS value, in order to avoid over-fitting, since from that point the incorporation of additional LV does not explain further variance. Considering the high number of employed variables, substantial variable reduction was obtained for all the parameters. Several papers have shown a similar number of latent variables to be required for the adequate prediction of similar parameters, avoiding over-fitting (Moghimi et al., 2010, for SSC and acidity; Qiang et al., 2010, for DM; Ragni et al., 2012, for firmness and SSC). A good model should have low RMSEC and low RMSEP, high correlation coefficients and a small dif-ference between RMSEC and RMSEP (Liu et al., 2014). The best correlation between measured and predicted data was observed for soluble solids content showing an R^2 of 0.910 (Table 3/Fig. 3a). Similar results for prediction of SSC in kiwifruit by NIR analysis have been obtained by Moghimi et al. (2010) and by Chen and Han (2012), showing the R^2 of 0.930 and 0.909 respectively. However in those works the RMSEP was higher in comparison to data presented in this paper showing values of 0.259 and 0.811 respectively. Besides, it is important to keep in mind that a larger range of SSC was analysed in the present work. The other three parameters showed good correlation coefficients (greater than 0.772) for test set validation and greater than 0.788 for calibration (Table 3/Fig. 3b,c,d), with the D_w values being the worst predicted

Table 2 – Effect of pre-processing methods on the explained variance and number of principal components (PCs) for osmo-dehydrated kiwifruit slices. Test-set validation was performed.

Pre-processing method	No of variables	No of PCs	Explained variance (%)		Explained variance by PCs (%)					
			Calibration	Validation						
VN	1959	4	99.197	99.068	70	21	7	1		
MSC	1959	4	98.896	98.703	67	27	5	1		
2nd Derivative	1959	6	94.954	92.930	53	34	4	3	1	1

MSC, multiplicative scattering correction; VN, vector normalisation.

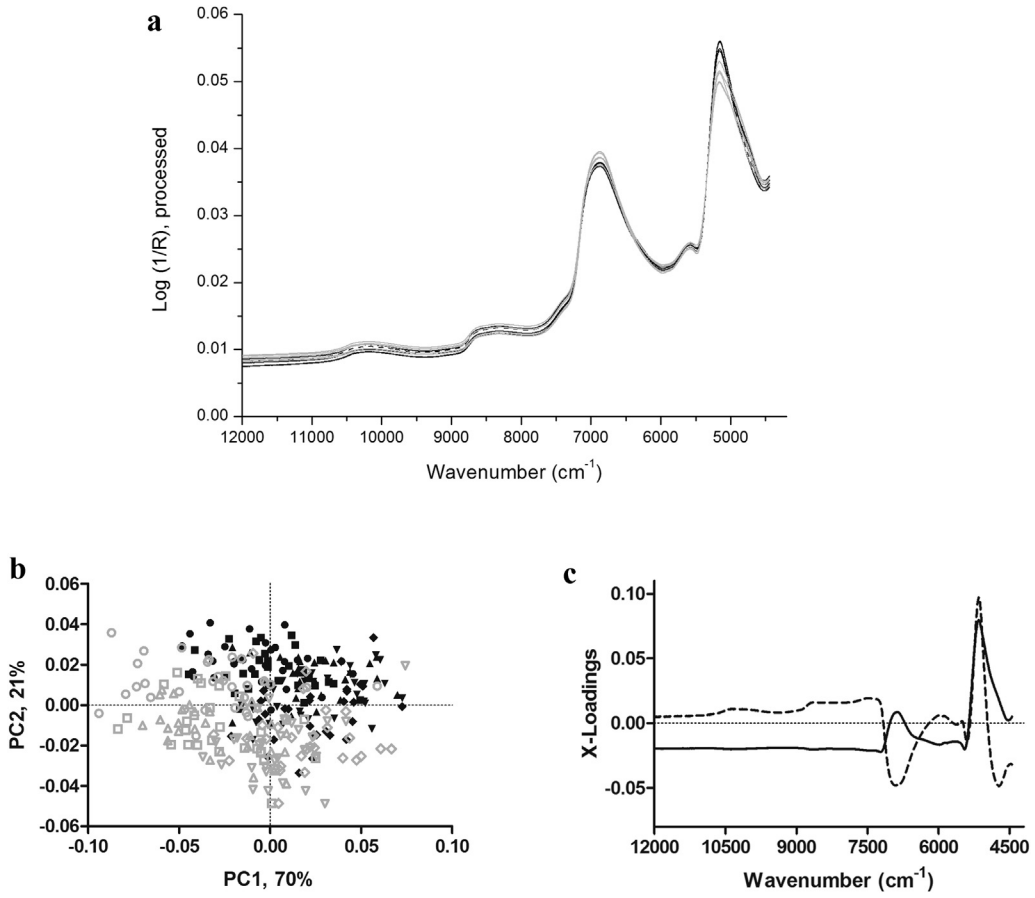

Fig. 2 – (a) Average NIR spectra of low (grey lines) and high (black lines) °Brix kiwifruit groups osmo-dehydrated for different times (0–300 min) after application of the vector normalisation pre-processing method; (b) the score plot of the two most significant principal components explaining 91% of the total variance [HB (black symbols) and LB (grey symbols) are low and high °Brix, respectively, and 0 (circles), 30 (squares), 60 (point-up triangles), 180 (point-down triangles) and 300 (rhomboids) are osmotic dehydration contact period in min]; (c) the X-Loadings *vs* wavenumber of the two most significant principal components (PC1: solid line; PC2: dashed line).

Table 3 – PLS regression models for predicting soluble solids content (SSC), dry matter (DM), diffusion coefficient by TD-NMR (D_w), and firmness (F). The regression models were applied to the dataset containing both kiwifruit groups (first four lines of Table). For firmness prediction only, the regressions were also applied separately for both low (LB) and high °Brix (HB) kiwifruit groups (last two lines of Table).

Parameter	Range	SD	Calibration			Test set validation				
			R^2	LV	RMSEC	R^2	LV	RMSEP	SEP	RPD
SSC (°Brix)	7.7–25.3	4	0.935	11	1.04	0.910	11	1.28	1.08	3.9
DM (% w $w^{-1}_{d.b.}$)	14.3–29.1	0.9	0.898	9	1.16	0.833	9	1.49	1.19	0.8
D_w (10^{-9} m^2 s^{-1})	1.10–1.77	0.05	0.788	12	0.06	0.772	12	0.06	0.06	0.8
F (N)	5–151	10	0.896	12	13.93	0.883	12	15.15	14.36	0.7
F, LB (N)	23–151	16	0.795	11	11.14	0.683	11	14.86	11.8	1.3
F, HB (N)	5–37	4	0.722	6	3.65	0.713	6	3.86	3.78	1.0

SD, standard deviation; LV, used latent variables; RMSEC, root mean square error of calibration; RMSEP: root mean square error of prediction; SEP, standard error of prediction; RPD, residual predictive deviation value of prediction. The number of variables (wavelengths) used was the same for all the parameters (1959). Vector normalisation was performed prior to regression.

among those studied. NIR spectroscopy is therefore valuable for firmness determination, which changes during OD treatment. The single model taking into account both kiwifruit groups showed a R^2_{val} of 0.883. However, Fig. 3d reveals a clear separation between the two kiwifruit groups and some predicted firmness values are negative (which have no sense). In order to improve the prediction capacity, two separate PLSR were conducted for LB and HB kiwifruits for the firmness parameter (Table 3, lines marked F, LB and F, HB; and Fig. 4). Applying two separate models gave lower SEP values than the

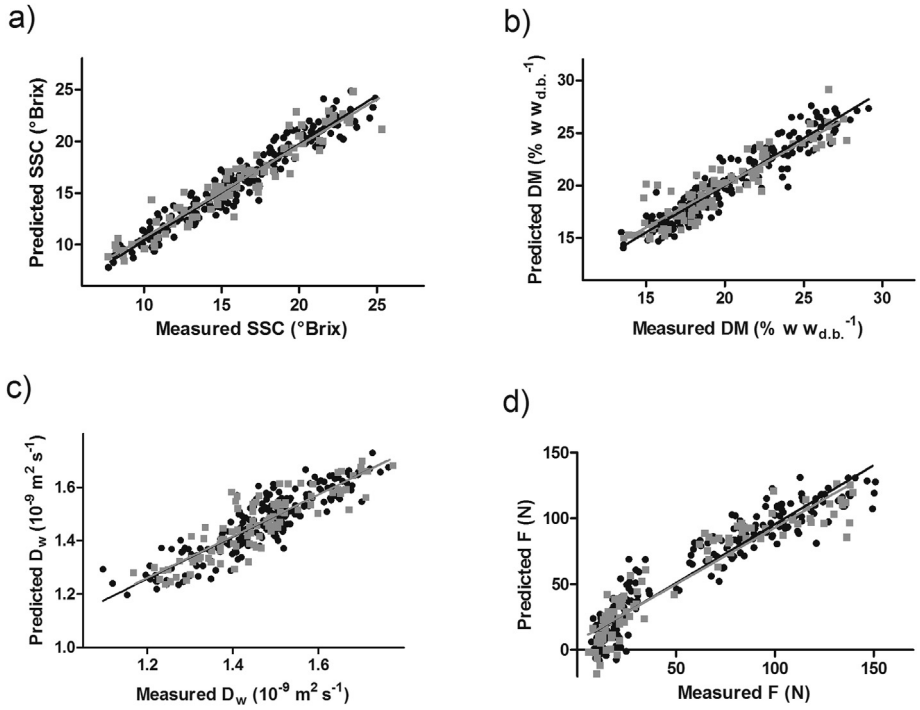

Fig. 3 – Measured *vs* predicted values for the prediction of (a) soluble solids content (SSC), (b) dry matter (DM, expressed in dry basis), (c) water self-diffusion coefficient (D_w), and (d) firmness (F) by PLSR model. Calibration set (black circles and black regression line) and prediction set (grey squares and grey regression lines) data are shown.

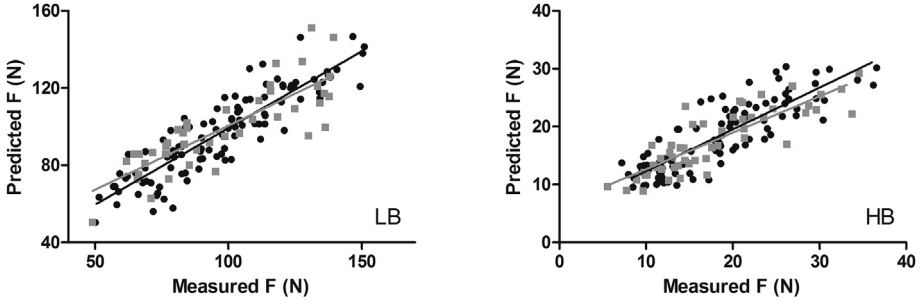

Fig. 4 – Measured *vs* predicted values for the prediction of firmness (F) by PLSR models applied to the low and high °Brix kiwifruit groups (LB and HB, respectively). Calibration set (black circles and black regression line) and prediction set (grey squares and grey regression lines) data are shown.

SD values (Table 3). Thus, even though the R^2 values were better for the single model, the separate models improved the accuracy of the firmness prediction when compared to the single model.

The residual predictive deviation (RPD) showed values in the range 0.7–3.9 (Table 3). According to Williams and Norris (2001), RPD value of a predictive models should be at least equal to 5 and if lower than 3, the regression model can be applied for rough screening. However all PLSR models showed SEP values comparable with the accuracy (SD values in Table 3) of the destructive methods traditionally used to measure these kiwifruit properties. Ragni et al. (2012) obtained RPD values around 2.2 for both SSC and Magness-Taylor fresh firmness on kiwifruit by waveguide spectroscopy, concluding that even though the models' accuracy was not high, the method was undoubtedly advantageous for the simultaneous assessment of these quality indexes. Several factors affects model success including the evaluated range (and the associated coefficient of variability), changes in fruit physiology over time, degree of ripening, and sample treatment and handling (or not) of the slices/fruits. As commented by Travers, Bertelsen, and Kucheryavskiy (2014), the complexity of absorbance spectra for DM and SSC plus their strong correlation suggests that prediction models cannot easily distinguish between soluble and non-soluble forms of carbohydrate, affecting differentially the model success.

The present paper has shown that, by a single NIR measurement, it is possible to successfully estimate four valuable technological/physico-chemical parameters in a rapid, non-destructive and accurate way, which could be useful to take rapid decisions during fruit processing. Specifically the online application of NIRS acquisition during OD treatment of raw

materials with variable characteristics, e.g. due to different ripening stage, may allow the process parameters to be adjusted rapidly to achieve the desired standardised characteristics of the final product.

4. Conclusions

This study shows that, as a non-destructive and rapid method, NIRS was able to determine the changes caused by OD on kiwifruit at different ripening stages.

Predictive models were successfully built by means of PLSR analysis. The application of vector normalisation pre-processing was critical to eliminate spectral information not related to the OD process.

Actually, once the calibration is performed, the acquisition of NIR spectrum of kiwifruit sample allows high precision estimation (with SEP values lower than the SD values obtained by more traditional methods) of relevant physico-chemical parameters of the product such SSC, DM, D_w and firmness. Even though the physico-chemical parameters still remain as a reference for quality determination, the possibility to determine these parameters altogether (after calibration) could have an enormous impact. Since NIRS is applied during on-line processing, this study shows that NIRS could be a very useful tool for the on-line optimisation of OD process parameters (e.g. time, temperature) for a particular product (defined by quality parameters such as those studied here) as a function of the ripening stage of the raw material.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biosystemseng.2015.12.011.

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