REAL-TIME MONITORING OF ORGANIC CARROT (VAR. *ROMANCE*) DURING HOT-AIR DRYING USING NEAR-INFRARED SPECTROSCOPY

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1.0 INTRODUCTION

Market globalization ensures constant availability of many horticultural products regardless of their harvest date. Innovation in both products and processes across the entire agri-food chain yield fruit and vegetables with improved shelf-life, organoleptic quality, nutritional value, safety and healthfulness. Consequently, preservation methods that enhance food stability by delaying physicochemical, biochemical and microbiological spoilage impact the market value of perishable commodities (Aghbashlo et al. 2015). In fact, preservation method directly affects processing, storage, transportation and distribution costs.

Drying is an effective and viable preservation process and is among the oldest and most widespread of all postharvest operations. Drying significantly extends the shelf-life and nutritional quality of fruit, vegetables, spices and herbs as well as meat and fish. The drying process consists of three main interlinked steps that can be summarized as: (1) product formulation or treatment selection, (2) dehydration process and (3) quality and properties assessment (Aghbashlo et al. 2015). In the

absence of sufficient moisture, microorganisms grow slowly and moisture-mediated reactions responsible for undesirable chemical changes do not function properly (Mayor and Sereno 2004; Demirhan and Özbek 2009). Beyond extending shelf life, drying can substantially reduce storage and shipping costs by enabling storage at room temperature and reducing weight and packaging volume (Liu et al., 2016, Grabowski et al., 2003).

Drying technology varies from simple methods such as sun drying to more sophisticated techniques such as instant controlled pressure drop drying. Surprisingly, modern drying technology does not always produce the highest commodity quality or value. Drying is a relatively complex, dynamic, unsteady and nonlinear process that is affected by the properties of the wet material, the scale of production and compliance with regulations (e.g. European Organic Regulation), as well as operating and environmental conditions (Aghbashlo et al. 2015). Such factors can impact quality traits including colour, texture, size and shape as well as organoleptic, nutritional and functional properties and thus result in reduced consumer acceptance (Brosnan and Sun 2004; Vega-Gálvez et al. 2012). Drying is one of the most energy-intensive processes in the food industry (Akpinar et al. 2003) and potentially contributes to climate change as most dryers use fossil fuels (Mujumdar 2012).

In order to alleviate these issues, the goal of new drying technologies should be to simultaneously maintain product quality and value, maximize drying rate and minimize environmental impact (Mujumdar 2012; Su et al. 2015). “Smart drying”, one of the newest and most promising of emerging drying techniques, involves the use of sensors, tools (e.g. emerging non-destructive technologies) and practices (e.g. monitor and control of quality and drying parameters and/or the conditions of the dryer, etc.) for enhancing drying efficiency. Moreover, smart drying can be cost-effective in both real-time monitoring of food quality and dynamic controlling of operating conditions through the entire drying process. Smart drying is a multi- and inter-disciplinary sector and its recent developments embrace the following R&D areas: artificial intelligence (Aghbashlo et al. 2015), biomimetic (Ghasemi-Varnamkhasti et al. 2010), computer vision (Brosnan and Sun 2004), microwave/dielectric spectroscopy (Jha et al. 2011), hyper-/multispectral imaging (ElMasry and Sun 2010), magnetic

resonance imaging (Clarka et al. 1997; Su et al. 2014), ultrasound imaging (Awad et al. 2012), electrostatic sensing (Chen et al. 2013) and control systems for the drying environment. In addition, visible (Vis) and near-infrared (NIR) spectroscopy are techniques with potential applications in smart drying in terms of monitoring quality attributes (Nicolaï et al. 2007). Furthermore, NIR spectroscopy is a proven on-/in-line tool with high sensitivity to changes in moisture content, particle size and the chemical state of food (Ozaki et al. 2006).

Carrot (*Daucus carota* L.) is one of the most nutritious root crops because of its high vitamin, ß-carotene and fiber content (Demiray and Tulek 2014). Dried carrot is an important raw material for the production of ready-to-eat meals such as instant powdered soups, sauces, spices, seasonings, etc. (Sánchez-Sáenz et al. 2015), which have become popular in the diet of modern consumers (Yi et al. 2015) in parallel with the human consumption of organic products (FAO 2011). Although carrot quality may be negatively impacted at high temperatures (Demiray and Tulek 2014), it is often blanched in hot-water and then dried using hot-air with the potential for subsequent loss of quality. Beyond quality degradation, conventional uncontrolled methods such as hot-air drying or freeze-drying are associated with a number of drawbacks, such as very long drying time and high energy demand (Mujumdar 2012). Thus, while proper selection of postharvest treatments both before and after carrot drying is critical, careful consideration and monitoring of appropriate drying techniques is also a crucial factor to obtain a high-value end product (Negi and Kumar Roy 2001).

The European Organic Regulation on production and labelling of organic products (i.e. EC No. 834/2007 and EC No. 889/2008) prohibits certain conventional drying treatments for organically grown carrots (e.g. use of restricted chemicals, microwave blanching, etc.). In this case smart drying technologies have the potential to optimize allowed drying processes to obtain comparable results to conventional methods.

While research into carrot drying has been widely reported, little insight is available on smart drying technology applied to carrots, and research of its potential use in the organic sector is totally lacking. Therefore, the objective of this study was to demonstrate the use of near-infrared (NIR)

spectroscopy as a smart drying technology that can non-destructively detect and monitor quality changes in organic carrot slices, blanched and not blanched, during hot-air drying.

2.0 MATERIALS AND METHODS

2.1 Sample preparation

Organic carrots (*Daucus carota L.*, var. Romance) were purchased from a local organic trader (Biobox srl, Viterbo, Italy) and immediately stored at 4 ± 1 °C until processing. Sampling was performed by selecting sound carrots with uniform size and thus the same ripening stage. Roots were tempered to room temperature for 15 h before use. The batches were standardised by selecting carrots with a length of 18-20 cm and diameter of 1.5-2 cm. Carrot slices, without core and peel, were prepared by washing and cutting the root into slices (5-mm thick) using a sharp ceramic knife. Samples were visually evaluated and only carrot slices free of decay and/or blemishes were selected for hot-air drying tests. Samples were divided into two groups, one of which was subjected to a hot-water blanching pre-treatment at 95°C for 1.45 min before hot-air drying and one that was dried without pre-treatment. Determination of appropriate blanching time and temperature is described in detail below.

Two hundred seventy carrot slices for each treatment were randomly arranged into 9 batches of 30 samples for the use in drying experiment. Then, carrot slices were subjected to 8-h hot-air drying and batch sampling was performed at 0, 1, 2, 3, 4, 5, 6, 7 and 8 h drying. Each batch was subjected to both NIR spectral data acquisition and determination of CIELab colour, moisture content (wet basis), water activity (a_w), soluble solids content and total carotenoid content.

2.2 Hot-water blanching pre-treatment

Hot-water blanching consisted of dipping carrot slices in hot-water using a temperature controlled water bath (Astor 800D, Astori Tecnica, Brescia, Italy). As a control (i.e. unblanched treatment), carrot slices were dipped in distilled water at room temperature.

2.3 Determination of blanching parameters based on peroxidase activity

The experimental plan is reported in Table 1. Treated samples were immediately cooled for 3 min in ice-water, and the residual Peroxidase (POD) enzymatic activity was evaluated.

2.3.1 Enzyme extraction

Enzyme purification was carried out on the basis of the method of Massantini et al. (2009) with some modifications. Carrot slices were collected after each blanching treatment, frozen with liquid nitrogen and then immediately ground into frozen powder using an analytic mill (IKA A11 basic; IKA Labortechnik, Staufen, Germany). Three grams of carrot powder were homogenized with 15 mL of chilled phosphate buffer solution (PBS, 0.1 mol L^{-1}, pH 6.5) containing 3% (w/v) of polyvinylpolypyrrolidone. The mixture was centrifuged at 13,800 × g for 20 min at 4 °C and the supernatant was used in the experimentation.

2.3.2 Enzyme activity measurement

POD activity was measured following the method of Moscetti et al. (2012) with slight modifications. The assay was performed using an UV-Vis scanning spectrophotometer (Lambda 25; PerkinElmer, Massachusetts, United States). Changes in the absorbance at 460 nm were monitored for 3 min upon oxidation of the substrates catalysed by the enzyme. Guaiacol (Sigma-Aldrich, St. Louis, Missouri, United States) was used as substrate. The final reaction mixture contained 1 mL of crude enzyme, 1 mL of PBS (0.1 mol L^{-1}, pH 6.5), 1 mL of guaiacol (0.25% v/v) and 0.01 mL of hydrogen peroxide (0.75% v/v). One unit of enzyme activity (1 UEA) was defined as an increase in absorbance of 0.001 min^{-1}. Enzyme activity was measured in triplicate.

2.3.3 Enzyme thermal inactivation

The rate constant for first-order inactivation (k) was computed from the slope of the linear regression of the natural log of residual activity versus time of thermal treatment, according to Eq. 1

$$\ln(E_t / E_0) = -kt \quad (1)$$

where E_0 is the initial enzyme activity (UEA), E_t is the activity after heating for time t (UEA), t is the time of heating (min) and k is the inactivation rate constant (min^{-1}). The regression coefficient (R) of each regression line was also computed.

A POD inactivation of 90% was fixed as a threshold in order to consider the produce stable for the industrial requirements (Benlloch-Tinoco et al. 2013). Consequently, inactivation time was computed as *D-value* (or decimal reduction time) as treatment time required to reduce the enzyme activity to at least 0.1 (i.e. 10% of its original value), according to Eq. 2.

(2) $$E_t / E_0 = E_0(1/2)^{t/t_{1/2}}$$

2.4 Hot-air dehydration process

The hot-air drying experiment was performed in a 5-tray dryer (Biosec, Tauro Essicatori srl, Vicenza, Italy). The dryer consisted of a temperature controller and a centrifugal fan that was used to blow air into the heating unit through a 15-cm duct. The air flow was parallel to the drying surface of the carrot slice. The dehydration process was conducted at 40°C for 8 h on the basis of screening results obtained from tests conducted in the range from 40 to 60 °C. Drying tests at temperatures higher than 40 °C were discarded due to an excessive case hardening effect and the development of a very compact structure. The investigation is in agreement with Xiao et al. (2010).

2.5 Near infrared spectroscopy

2.5.1 Spectral acquisition

Diffuse reflectance spectra were acquired using a Luminar 5030 Acousto-Optic Tunable Filter-Near Infrared (AOTF-NIR) Miniature 'Hand-held' Analyzer coupled with the bundled 'SNAP! 2.04' software (Brimrose Corp., Baltimore, USA). The instrument was equipped with a reflectance post-dispersive optical configuration, a pre-aligned dual beam lamp assembly and an indium gallium arsenide (InGaAs) array (range 1100-2300 nm, 2-nm resolution) with an integrating time of 60 msec. The reference spectrum was automatically measured by the instrument following the method used by (Moscetti et al., 2015a). Each sample was measured in duplicate on two opposite sides of each carrot slice (i.e. 4 spectra per sample). Reflectance spectra were converted to absorbance ($A = \log R^{-1}$) and the average spectrum was used for further computations.

2.5.2 Spectral pre-treatments

Each carrot slice was modelled as a 'data vector', where the spectral absorbance values (otherwise called features) were vector components. Chemometric analysis was performed following spectral pre-treatments including Standard Normal Variate (SNV), Multiplicative Scatter Correction (MSC), and Savitzky-Golay first and second derivatives (*D1f* and *D2f*, respectively) with a second or third order polynomial fitted over a window of five (S5), seven (S7), nine (S9) or eleven (S11) features (Savitzky and Golay 1964; Boysworth and Booksh 2008). For each dataset, Mean Centering (MC) was also tested as spectral pre-treatment. Every possible combination of pre-processing was also tested and only best results, in terms of model performances, were retained.

2.5.3 Prediction of chemical and physicochemical changes (regression models development)

Regression models were computed using the partial least squares (PLS) regression through the SIMPLS algorithm (de Jong 1993). PLS is a regression technique used to find useful linear combinations of the original independent variables, thus discarding irrelevant and unstable information, solving any problems with collinearity and, finally, obtaining a more stable regression. In addition, the Interval PLS (iPLS) algorithm was also used to select a subset of wavelengths which could achieve superior prediction compared to PLS models based on all features dataset (Xing et al. 2008). The iPLS algorithm was configured in stepwise forward mode for the selection of a maximum of 10 wavelengths.

As PLS and iPLS regressions perform a dimensionality reduction, it is essential to test each model and select the correct number of latent variables to find the optimal trade-off between under-fitting and over-fitting. Thus, the samples were randomly split as follows: 75% and 25% of the samples were assigned to the calibration set (C) and the prediction set (P), respectively. Every PLS and iPLS model was optimized by computing a venetian blinds cross-validation with 10 data splits. This cross-validation method was preferred because it is simple and easy to implement, relatively fast, generally safe and capable of providing a better representation when the dataset contains many samples, as is the case here (Naes et al. 2004; Wise 2009). Root Mean Square Error for calibration, cross-validation and prediction calculations (RMSEC, RMSECV and RMSEP, respectively) were

employed to evaluate each regression model with the purpose of selecting the optimal number of latent variables and thus circumvent unrealistic results (Moscetti et al. 2015b). Model performances were also evaluated in terms of BIAS and coefficient of determination (R^2).

PLS and iPLS models were both computed to predict changes in chemical and physicochemical attributes during 8-h dehydration process.

2.5.4 Prediction of the drying phases (classification models development)

Classification models were developed using K-means and Partial Least Squares Discriminant Analysis (PLS-DA) algorithms in sequence (Fig. 1). As the initial step, K-means was employed to determine the number of drying phases (i.e. classes) and to label each sample as belonging to a specific class on the basis of the observed changes in moisture content, water activity, CIELab colour and soluble solids content. K-means is a partitional clustering method belonging to the group of the unsupervised hierarchical cluster analyses. The selection of the most appropriate cluster solution was performed by computing both actual and random sum of square errors (SSE) for a maximum of 9 clusters (i.e. 9 times of dehydration). Random SSEs were computed from 300 randomized versions of the original dataset. To determine the optimal cluster level, the scree plots of both (1) the actual SSE versus the cluster solutions and (2) the difference between the actual and random SSEs against the cluster solutions, were investigated. The best cluster level was chosen as solution at which the plot of the actual SSE versus clusters produced an "elbow" and the actual SSE differed the most from the average of the random SSEs.

As a final step, the identified class membership was used as the response variable (Y) for the development of PLS-DA models in which the predictor variables (X) were spectral profiles. Thus, PLS-DA was used to assign each carrot slice to a specific dehydration phase on the basis of its spectral profile. Moreover, the Interval PLS-DA (iPLS-DA) algorithm was used to identify and test a maximum of 10 features. As in the PLS regression model, the RMSE analysis was performed to select the optimal number of latent variables also for both PLS-DA and iPLS-DA classification models (Goodarzi et al. 2013). The classification performance of each PLS-DA and iPLS-DA model was

determined in terms of sensitivity (Eq. 3), selectivity (Eq. 4) and accuracy (Eq. 5) rates (Dejaegher et al. 2011). The accuracy rate was used to mainly select models in terms of predictivity, while sensitivity and specificity rates were jointly employed to perform a model sub-selection in terms of robustness (i.e. the capability of the model to resist to small changes in test conditions).

(3) $$Sensitivity\ rate = \frac{True\ Positives}{True\ Positives + False\ Negatives}$$

(4) $$Selectivity\ rate = \frac{True\ Negatives}{False\ Positives + True\ Negatives}$$

(5) $$Accuracy\ rate = \frac{True\ Positives + True\ Negatives}{Total\ Positives + Total\ Negatives}$$

As previously described for the development of regression models, the dataset was randomly split in calibration and prediction sets (75% and 25% of samples, respectively) and every PLS-DA model was optimized by computing a venetian blinds cross-validation with 10 data splits.

2.6 Chemical and physicochemical attributes

Both chemical and physicochemical attributes were measured immediately after the NIR spectral acquisitions. Carrot slice colour was measured with a spectrophotometer (CM-2600d, Konica Minolta, Osaka, Japan) with CIE Standard Illuminant D65 (Daylight), Observer 10° and 6-mm diameter of measurement aperture mode. Four replications were performed for each sample by performing two colour measurements on two opposite sides of each carrot disc. The results were expressed according to the CIELab colour space and thus in terms of lightness (L^*), redness (a^*), yellowness (b^*), hue angle (h) and chroma (C^*) (Moscetti et al. 2013).

Moisture content was measured following the official method 'Moisture in Dried Fruits' - AOAC 934.06 and was expressed as a percentage by mass (grams per 100 grams) (Horwitz 2005).

Water activity (a_w) was determined with an Aqua Lab (3TE, Decagon Devices Inc., Washington, USA).

Soluble solids content (SSC) was measured with a digital refractometer mod. WM-7 (Atago, Tokyo, Japan) by following the method of Lavelli and Kerr (2012) with slight modifications. The

vortexed and centrifuged extract of 350 mg of freeze-dried sample with 10 mL of distilled water was measured. Results were then converted on a fresh weight basis and expressed as °Brix (grams of sucrose per 100 g of fresh product).

Carotenoids were extracted by incubating 500 mg of freeze-dried carrot tissues in 10 mL of 2:1:1 hexane, acetone and ethanol mixture for 24 h at room temperature in darkness. The total carotenoid content was determined by measuring absorbance at wavelength of 450 nm, using the Eq. 6 (Scott 2001).

$$\mu g\ carotenoid\ mL^{-1} = \frac{A \times V_1}{A^{1\%}} \times C^{1\%} \quad (6)$$

where A is the absorbance reading of the sample, V_1 is the dilution factor, $A^{1\%}$ is the extinction coefficient of the 1% solution (i.e. 2500 AU) and $C^{1\%}$ is the concentration of the 1% solution (10 mg mL^{-1}). The total carotenoid content was converted in μg g^{-1} of fresh tissue.

Analyses were performed in triplicate.

2.7 Data handling and data mining

One-way analysis of variance (ANOVA) was performed to evaluate statistical differences among the drying times. The Tukey's pairwise comparison method was performed, and the Honestly Significant Difference (HSD) was calculated for an appropriate level of interaction ($P \leq 0.05$) (Montgomery 2001). Results were reported as the mean and deviation standard of the mean. Before statistical analysis, results relative to moisture content were subjected to angular transformation (i.e. y = arcsine $[x]^{1/2}$) to homogenize the variance (Bartlett's test) (Gomez and Gomez 1984). The data reported were back transformed.

Data handling and ANOVA were both performed using R v3.3.3 software in combination with 'dplyr' v0.5.0 and 'agricolae' v1.2-4 R-packages (CRAN 2017). Chemometrics was performed using Matlab software R2015a coupled with PLS_Toolbox software v8.1 (Eigenvector Research Inc., WA, USA).

3.0 RESULTS AND DISCUSSION

In the present work, the carrot drying process was monitored using NIR spectroscopy. NIR-based regression and classification models were computed and the impact of the hot-water pre-treatment as enzyme inactivator on model performance was also investigated.

3.1 Thermal pre-treatment selection

The effect of thermal treatment on carrot slices was evaluated for hot-water blanching over the pre-established range of temperature (Table 1). To monitor the thermal treatment, peroxidase was used as indicator enzyme due to its higher thermal stability and easiness in being assayed. In fact, the POD inactivation allows the reasonable assumption that other quality-deteriorative enzymes (e.g. pectinesterase, lipoxygenase, etc.) are also inactivated (Sergio et al. 2007).

Inactivation kinetics was determined through semi-log plot of residual POD activity versus time. Results showed excellent linear fits (R = -0.98÷-1.00) at all temperatures studied, consistent with inactivation occurring by first-order kinetics (Fig. 2). Although all treatments reached the inactivation threshold (decimal reduction, 90%), considerably faster reductions in POD activity were only achieved at 90 and 95°C. In fact, both hot-water blanching at 80 and 90°C were less effective, showing slowest inactivation rate constants (k) (0.20 and 0.57 min^{-1}, respectively) in comparison with 90 and 95°C (0.77 and 1.60 min^{-1}, respectively). Moreover, hot-water blanching at 90 and 95°C led to more vivid and pleasant colour (data not shown). Similar results were reported by Sims et al. (1993) and Bao and Chang (1994), which observed greater hue angle and chroma, and thus better colour than those from unblanched carrots. The colour of carrots is deeply affected by the presence of α- and ß-carotenes, which are known to be relatively heat-stable at combination of temperature and time used in our experiments (Behsnilian and Mayer-Miebach 2017). In fact, carotenoids degradation and isomerization into *cis*-isomers are responsible for loss of vivid colour and a shift from orange to more red colour (Howard et al. 1996), which is not our case.

Finally, the lowest decimal reduction time (D) among treatments was achieved by using hot-water blanching at 95°C for 1.44 min of dipping. Thus, considering that the evaluation of the effects of treatment on nutritional value of product was not part of the present study, hot-water blanching at

95°C for approx. 1.45 min was selected as the most adequate treatment to obtain colour-stable carrot slices to use further in the experimentation.

3.2 Spectral data overview

Fig. 3 depicts the resulting mean relative absorbance spectra obtained from the AOTF-NIR spectrophotometer in the 1100-2300-nm spectral range. Fig. 3a and 3b provide information about spectral differences between treatments (i.e. control and blanching treatments, respectively) and among drying times. Changes in the spectral profiles during the drying process were evident to the naked eye for both control and blanching treatments. In fact, it should be noted that drying time heavily affected the spectral characteristics in the water absorption bands (1450 and 1940 nm) (Saeys et al. 2008) and, more generally, in the higher wavelength region (1900-2300 nm), which is notably associated with carbohydrates, sugars and proteins (Ambrose et al. 2016). On the other hand, blanched samples apparently showed more changes in spectral shape during the drying process and pronounced shoulders on either side of the two principal water absorption bands (1450 and 1940 nm). These results suggest that the differences in spectral profile should be mainly due to both water loss and changes in forward scattering and backscattering by flesh tissue as a consequence of the blanching treatment.

3.3 Chemical and physicochemical changes during drying

Table 2 summarizes changes in chemical and physicochemical parameters on blanched and unblanched (i.e. control) carrot slices subjected to 8-h drying. ANOVA indicates a significant effect of drying time on each quality parameter. Moisture content and water activity gradually decreased during drying time, while both SSC and total carotenoids content increased due to decline in water content. Results were perfectly in agreement with those of other authors (Suvarnakuta et al. 2005; Lavelli et al. 2007; Markowski and Zielińska 2011). However, different drying behaviours between treatments were noted. In fact, blanched samples showed a faster decrease in moisture content during drying and a lower experimental variability for SSC, lightness and hue angle. The data also revealed that the colour of blanched carrot slices was significantly different from the untreated slices. Hot-

water blanching entailed a lower initial (0-h drying) and final (8-h drying) lightness (L^*) as well as a higher initial and lower final hue angle (h). Thus, hot-water blanching better retained the colour due to reduction in white blush. However, the variation in L^* value was not totally clear, similar to results reported by Krokida et al. (1998, 2001). Moreover, increased drying time was found to decrease hue-angle (h) when the hot-water blanching was applied.

The chemical and physicochemical features of 270 carrot slices per treatment were clustered using the K-means algorithm. A cluster analysis was performed in each treatment group. On the basis of the results obtained, the optimal cluster level was identified as three and thus samples were split into three main classes (also named 'Drying phase I', 'Drying phase II' and 'Drying phase III'), each one characterized by a specific drying period (Table 2). Results showed that the duration of drying phases did not differ between treatments. In fact, both treatments were characterized by the 'Drying phase I' starting from 0 to 2 h of drying, the 'Drying phase II' starting from 3 to 5 hours of drying and the 'Drying phase III' from 6 to 8 h of drying.

Data from the analysis of quality parameters and labels from the K-means analysis were both used as Y-vector for the development of regression and classification models, respectively.

3.3 Regression models

The complete calibration and prediction performances of the regression models are summarized in Table 3. Poor results ($R^2 < 0.70$) were obtained for the prediction of the soluble solids content for the unblanched treatment. Conversely, regression models with good ($R^2 \geq 0.80$), very good ($R^2 \geq 0.90$) or excellent ($R^2 \geq 0.95$) predictability were obtained to monitor changes in soluble solids content (only for blanched carrots); and a_w (Fig. 4a), moisture content (Fig. 4b), total carotenoids content (Fig. 4c) and colour changes (Fig. 4d) of carrot slices during drying, regardless of thermal treatment and number of features used in the model. In detail, except for calibration model for colour changes, the coefficient of determination (R^2) was higher than 0.90 for the aforementioned parameters. Thus, for the test set validation with one quarter of the data (randomly selected) RMSEPs ranging from 0.03-0.04 for a_w, 0.03-0.04 for moisture content and 22.62-29.51 for total carotenoids

content were obtained. Moreover, although results from colour analysis showed good fittings, development of colour prediction models was totally affected by the pre-treatment used. In fact, blanched samples showed the best fitting metrics in predicting changes in hue angle (*h*), while for unblanched carrot slices, which were prone to the white blush discoloration, multivariate models were successfully computed only for the monitoring of changes in lightness (*L**).

The aforementioned performance parameters were comparable with both calibration and cross-validation results. Moreover, models obtained from feature selection (i.e. iPLS model) usually allowed the use of a lower number of latent variables in comparison with a full-spectrum model (i.e. PLS model).

Although the colour models resulted in R^2 below 0.85, good performance were still obtained with RMSEP values ranging from 1.66 to 1.79 for the lightness (*L**) and from 1.34 to 1.46 for hue angle (*h*). Considering that the 1100-2300-nm spectral band is not directly related to colour information, results obtained by the indirect measurement of changes in both *L** and *h* can be considered acceptable. However, it can be speculated that by including the visible range the model performance might be improved considerably.

Generally, with respect to the treatment, iPLS algorithm led to a higher number of selected features for blanched samples, which also differed from the unblanched treatment in terms of selected wavelengths. Results suggest that the effect of hot-water blanching on water loss and changes in microstructure was pronounced, affecting the model development.

Table 3 also gives an overview of the spectral pre-treatments effectively used in the selected models. In general, reducing and/or removing uninformative variance from the raw spectral data was essential for the development of well-performing regression models as all best models use spectral pre-treatments. In fact, it can be inferred that SNV scatter correction was necessary to minimize the RMSE and thus obtain the highest R^2. This may mean that the variation in light scattering negatively interfered with spectral information related to chemical and physicochemical parameters. Savitzky-Golay smoothing improved the prediction performance for most of the regression models. Thus, the

need for smoothing suggests that spectral data were slightly affected by noise. Mean centering was effective in improving regression performance through spectral resolution enhancement; in fact, this technique led to superior results as compared to those obtained from non-mean-centered spectra (data not shown).

3.4 Classification models

The combinations of spectral pre-treatments, discriminant algorithms and features which gave the best classification performance for the assignment of each carrot slice to a specific drying phase on the basis of its spectral profile are summarized in Table 4. The optimal combination of spectral pre-processing treatments was similar to those previously selected for the development of regression models. Pre-treatment methods such as SNV (for baseline correction), Savitzky-Golay smoothing filter (for noise reduction) and Mean Centering (for resolution enhancement) were selected as best combination for removing/reducing unwanted background information (i.e. light scattering and noise arising from various physical and/or chemical processes).

All models yielded good (> 85%) to excellent (> 95%) sensitivity and specificity for all drying phases (i.e. 'Drying Phase I', 'Drying Phase II' and 'Drying Phase III'). Thus, the models had greater ability to discriminate between the classes with respect to another class. In particular, all models had the highest sensitivity and specificity for 'Drying Phase I' and 'Drying Phase III'. This indicates that the classification of carrot slices as belonging or not belonging to both initial and final drying phases was the most accurate. Moreover, it should be noted that the worst predictive ability was always paired to 'Drying Phase II'. This can probably be explained by the fact that the variation in the properties of carrot slices classified as 'Drying Phase II' was much higher than variation in properties of carrot slices classified as belonging to 'Drying Phase I' or 'Drying Phase III'. In addition, as already observed for the case of regression models, discriminant analysis classifiers using blanched carrots resulted in better prediction ability than those from unblanched samples.

Finally, models obtained from a reduced number of features (i.e. iPLS-DA) showed discriminant performances very similar to models computed from the full spectrum (i.e. PLS-DA).

Moreover, iPLS-DA models were always characterized by a higher variance explained by a lower number of latent variables (data not shown). This is confirmed by both Fig. 5a and 5b, which show pattern similarity between scores from PLS-DA and iPLS-DA models. Finally, yet importantly, the results demonstrated a remarkable effect of hot-water blanching treatment on the performances of both PLS-DA and iPLS-DA models. Moreover, feature selection seems to be affected by the thermal treatment as selected wavelengths were slightly different between treatments. Thus, prior to implementation in industry, this approach should be further validated on a larger sample size covering the most important variations expected from structural changes in carrots due to the effect of thermal treatment and drying process.

4.0 CONCLUSIONS

In this study, the potential of near-infrared (NIR) spectroscopy in the 1100-2300-nm spectral range was evaluated to proactively and non-destructively detect and monitor changes in quality parameters (i.e. water activity, moisture content, total carotenoids content, colours and SSC) of carrot slices (*Daucus carota L.* var. Romance) during hot-air drying. For this purpose, regression and classification models were developed and the impact of the hot-water blanching (at 95°C for 1.45 min) as enzyme inactivator on model performance was also investigated. Optimal features were also selected for both regression (PLS) and discriminant (PLS-DA) analysis by using the interval PLS algorithm configured in stepwise forward mode. Both iPLS and iPLS-DA models showed similar o better performances than model obtained using the full spectrum.

In general, both PLS and PLS-DA models obtained either very good or excellent results. Specifically for regression analysis, models characterized by remarkable performances were obtained for water activity (R^2 = 0.91-0.96; RMSEP = 0.03-0.04), moisture content (R^2 = 0.97-0.98; RMSEP = 0.03-0.04), total carotenoids content (R^2 = 0.92-0.96; RMSEP = 22.62-29.51 μg g^{-1} fresh sample), lightness for unblanched carrots (R^2 = 0.80-0.83; RMSEP = 1.66-1.79) and hue angle for blanched samples (R^2 = 0.85-0.87; RMSEP = 1.34-1.46). In addition, while soluble solids content was poorly predicted for both treatments (RMSEP = 3.43-4.40), blanched carrots showed better coefficients of

determination (i.e. $R^2 > 0.85$) than unblanched samples (i.e. $R^2 < 0.70$). Regarding the discriminant analysis, PLS-DA algorithms obtained high accuracy in classifying drying phases based on the spectral profile. However, better results were obtained for models computed using blanched carrots. Specifically, NIR spectroscopy showed an excellent classification accuracy (> 0.90) for carrot slices belonging to 'Drying phase I' and 'Drying phase III'. On the other hand, misclassified carrot slices were primarily assigned to 'Drying phase II', which however showed accuracy greater than 0.85. It should be noted that the development of regression and classification models were affected by the blanching treatment in terms of number of features, selected wavelengths and model performances. Consequently, the proposed method should be further validated to circumvent model robustness issues due to both water loss and microstructural changes in carrots due to thermal treatments.

Finally, the approach presented in this research lays the foundation for an accurate smart-drying system based on NIR spectroscopy in terms of regression and classification performances, non-destructive analysis and automation. However, the number of wavelengths required in an online drying device would depend on the spectral pre-treatment used. Consequently, future research should include wavebands not covered by the spectrophotometer used for this study, increasing the light-beam intensity, and/or combining other chemometric methods, as these could improve the performance and the robustness of the smart-drying system.

These promising results encourage additional research to develop low-cost dynamic multi factorial process control strategies (based on a Quality by Design approach) using machine learning architectures to produce quality dried products while reducing the environmental impact of the drying processes.

5.0 ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1. Flowchart of the development of classification model for drying phases detection using K-means clustering (unsupervised learning) paired to PLS-DA algorithm (supervised learning). (*) Unlabelled data corresponds to changes in water activity, moisture, colour and soluble solids content values collected during 8-h drying. (**) NIR labelled data corresponds to spectral data (X) acquired during 8-h drying and paired to class membership (i.e. response variable, Y) becoming from K-means.

Figure 2. Semi-log (a) and non-linear (b) first-order plots for carrot slices' peroxidase heat-inactivation at 70, 80, 90, and 95°C. D-value states for decimal reduction time, which is the treatment time required to reduce the residual peroxidase activity to at least 0.1.

Figure 3. Mean relative absorbance spectra for control (a) and hot-water blanching (b) treatments at different drying times (i.e. from 0- to 8-h drying with step of 1-h drying).

Figure 4. PLS regression plots of Y-measured (reference) and Y-predicted (NIR) values for water activity (column a), moisture (column b), total carotenoids content (column c) and colour changes (column d) monitored during 8-h drying in both unblanched (row 1) and blanched (row 2) carrots. PLS regression plots refer to models based obtained from the full spectrum.

Figure 5. Drying phases' spatial distribution plots obtained from PLS-DA (a) and iPLS-DA (b) models for '0-2 h', '3-5 h' and '6-8 h' classes (i.e. drying phases) of the unblanched treatment. Percentages of the explained variance are reported in parentheses on the axes. Red point with green outline corresponds to 'Drying Phase II' sample erroneously classified as belonging to 'Drying Phase I'. Green point with red outline corresponds to 'Drying Phase I' sample erroneously classified as belonging to 'Drying Phase II'. Green point with blue outline corresponds to 'Drying Phase III' sample erroneously classified as belonging to 'Drying Phase II'. Blue point with green outline corresponds to 'Drying Phase II' sample erroneously classified as belonging to 'Drying Phase III'.

Figure 1

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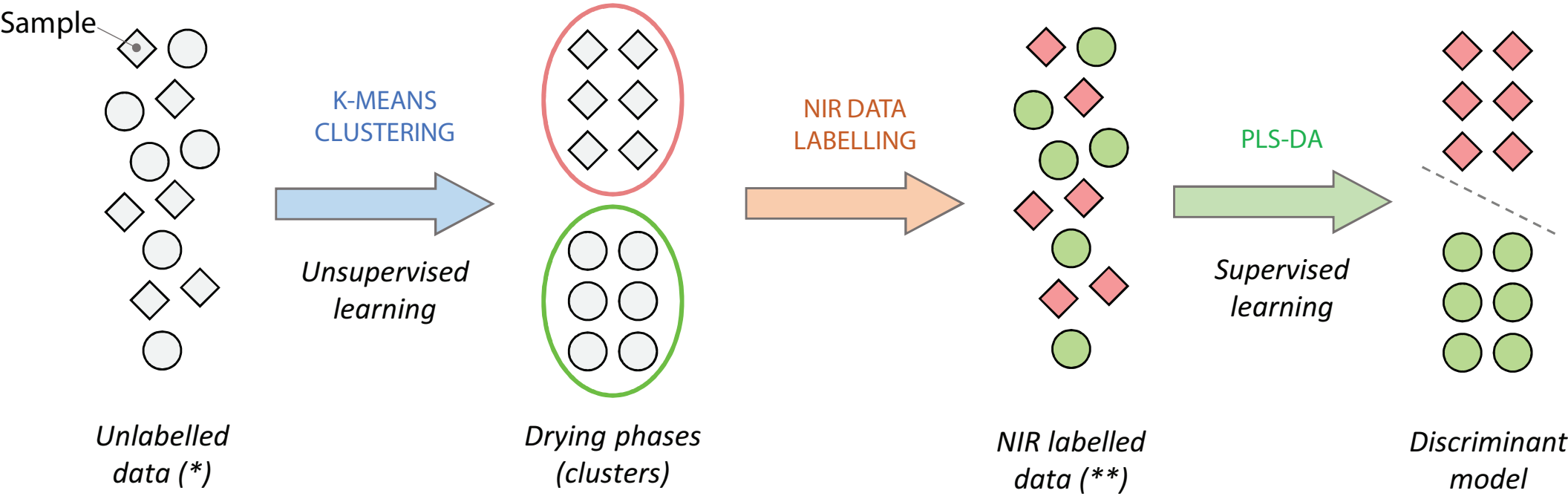

Figure 2

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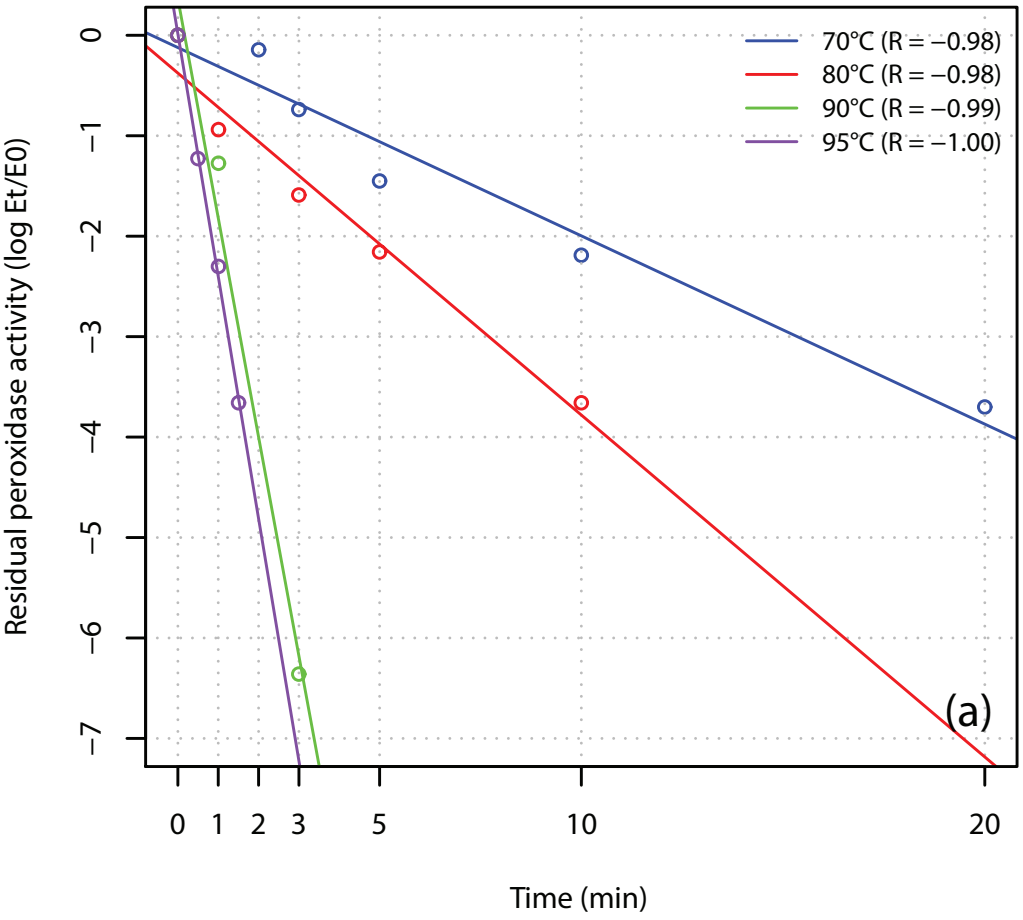

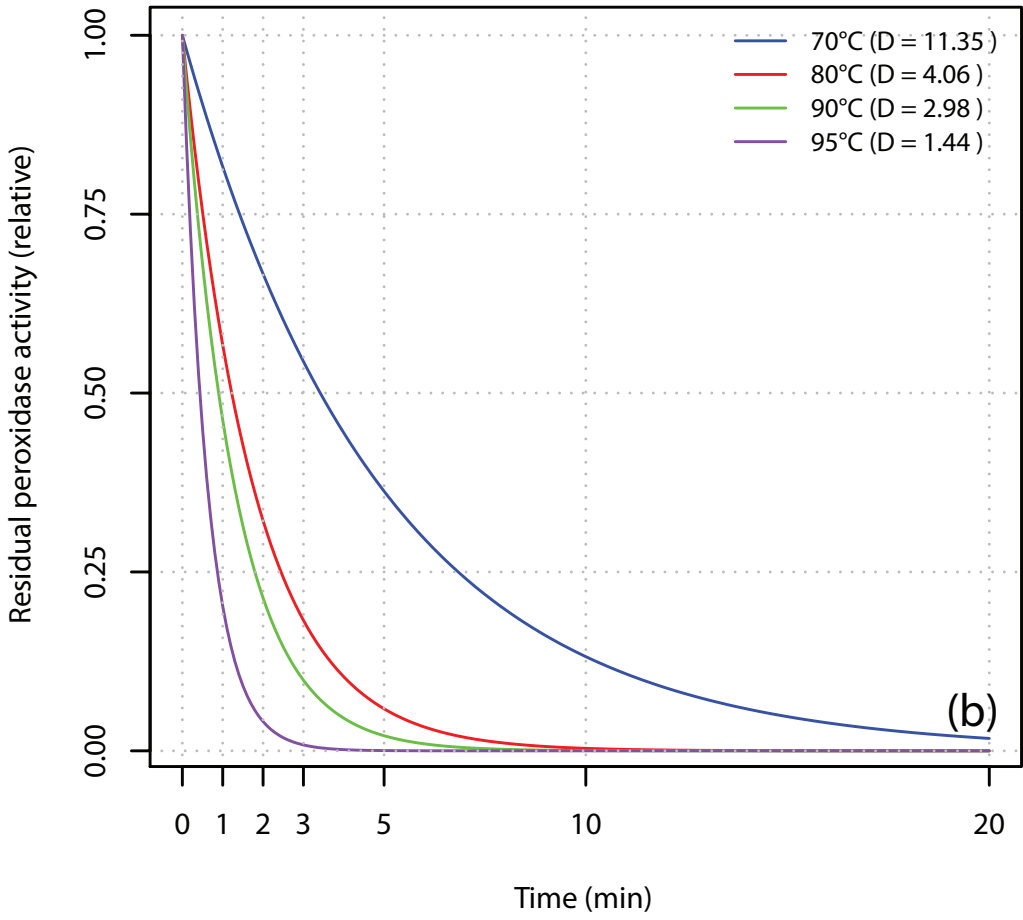

Figure 3

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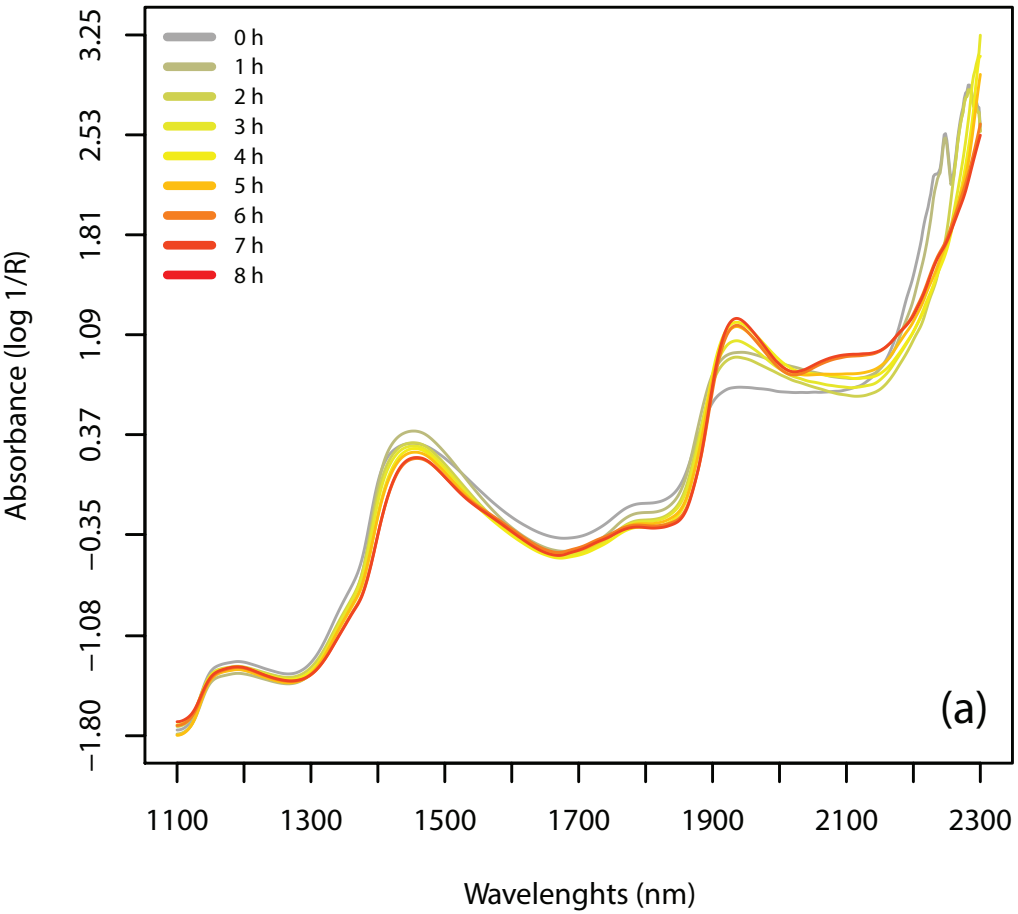

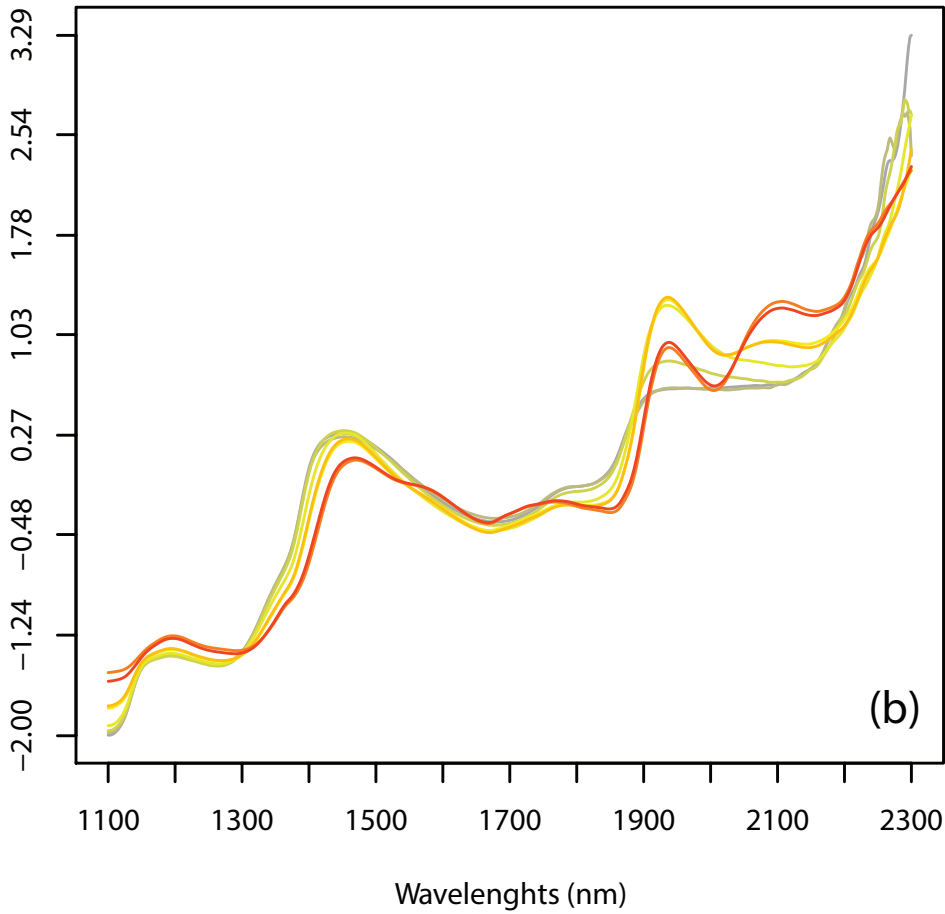

Figure 4

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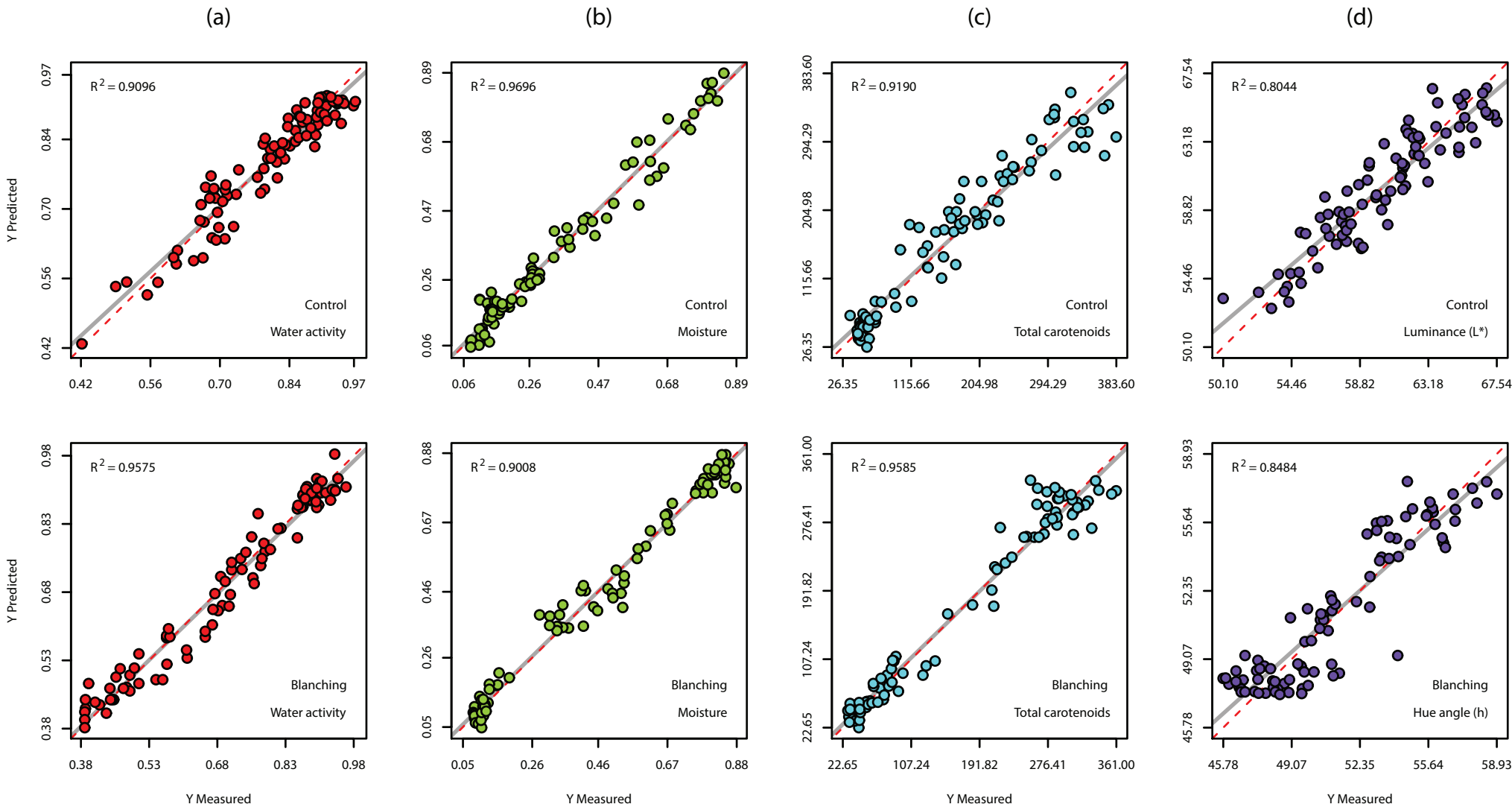

Figure 5

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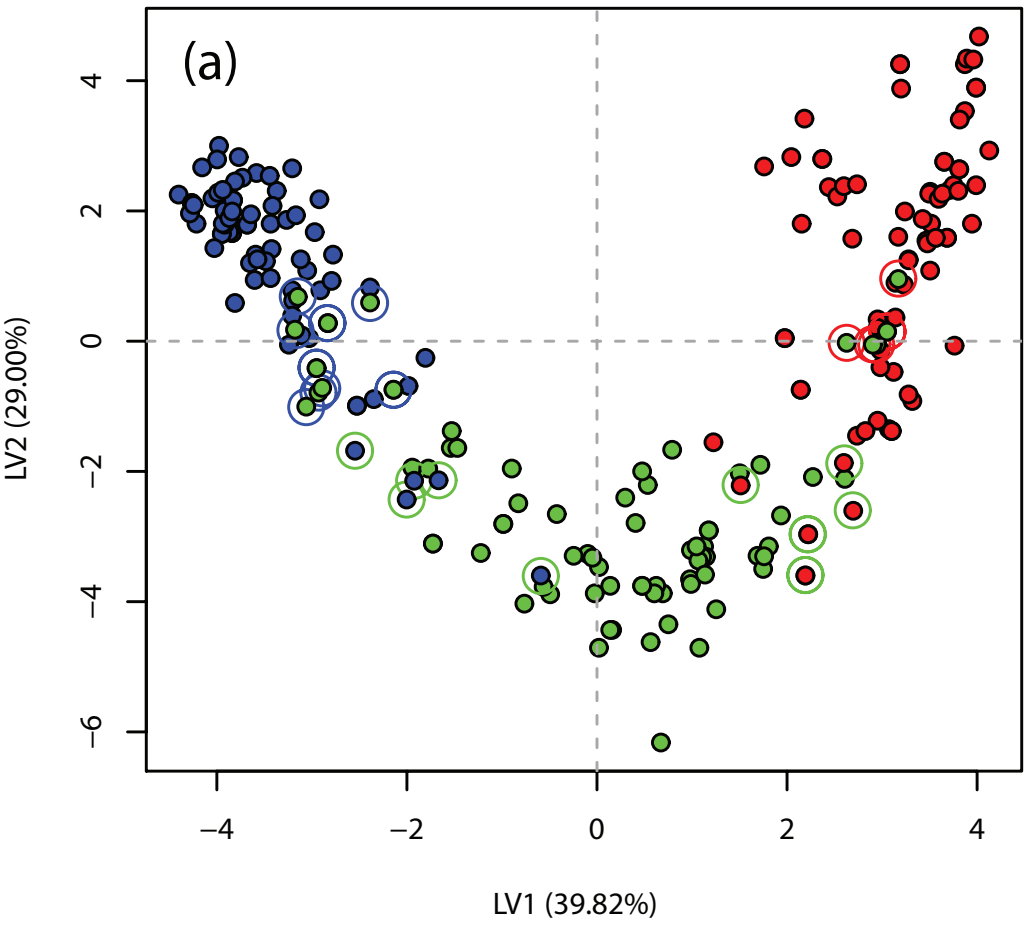

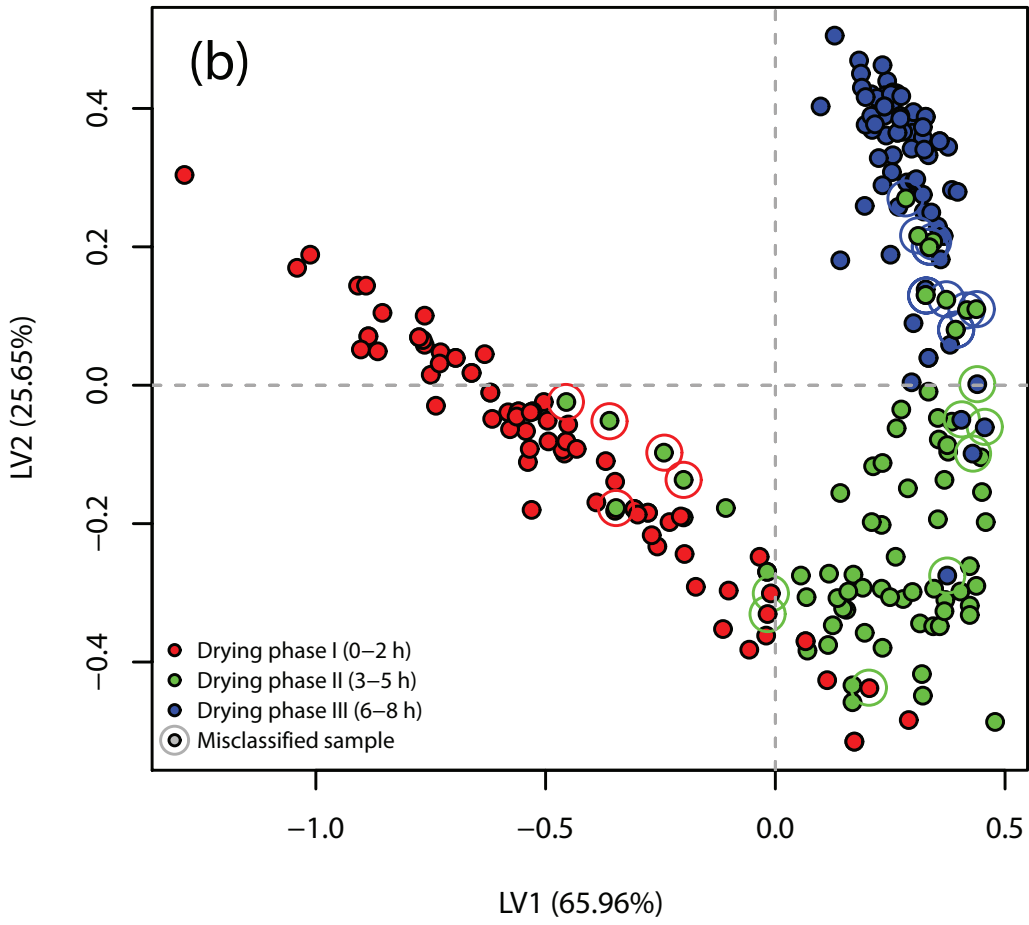

TABLE CAPTIONS

Table 1. Experimental design for the hot-water blanching treatment.

Table 2. Main effect of drying time on the chemical and physicochemical quality parameters of carrot slices. Mean values with no common letters are statistically different according to HSD ($p \leq 0.05$). Drying times were clustered in drying phases (i.e. I, II and III) according to the results obtained from the K-means cluster analysis.

Table 3. Summary of performance metrics for the combinations of treatment, spectral pre-processing and regression algorithm (i.e. PLS and iPLS) complexity which gave the best results during 8-h drying.

Table 4. Summary of performance metrics for the combinations of treatment, spectral pre-processing and classification algorithm (i.e. PLS-DA and iPLS-DA) complexity which gave the best results during 8-h drying.

TABLE 1

Temp. (°C)	Time (min)								
	0.0	0.5	1.0	1.5	2.0	3.0	5.0	10.0	20.0
70	✓	×	×	×	✓	✓	✓	✓	✓
80	✓	×	✓	×	×	✓	✓	✓	✓
90	✓	×	✓	×	×	✓	✓	×	×
95	✓	✓	✓	✓	×	×	×	×	×

TABLE 2

Treatment	Drying phase (K-means)	Drying time (hour)	Water activity (a_w)	Moisture (relative)	SSC (°Brix)	Lightness (*L**)	Hue angle (*h*)	Total carotenoids
Control	I	0	0.88 ± 0.04 a	0.90 ± 0.02 a	6.35 ± 1.43 f	53.61 ± 1.47 f	51.82 ± 0.37 bc	50.75 ± 3.05 d
		1	0.84 ± 0.04 ab	0.86 ± 0.01 ab	8.58 ± 0.99 ef	57.38 ± 1.36 e	53.43 ± 0.50 ab	52.90 ± 5.66 d
		2	0.82 ± 0.05 b	0.85 ± 0.01 ab	8.56 ± 1.27 ef	58.70 ± 1.60 de	53.32 ± 0.62 bc	66.26 ± 15.09 d
	II	3	0.64 ± 0.03 c	0.82 ± 0.03 b	10.57 ± 1.64 de	61.65 ± 4.28 bcd	50.40 ± 1.38 c	154.88 ± 37.01 c
		4	0.62 ± 0.03 c	0.67 ± 0.09 c	14.69 ± 3.15 bc	64.67 ± 2.14 ab	50.18 ± 0.95 c	205.63 ± 87.36 bc
		5	0.45 ± 0.03 d	0.72 ± 0.05 c	12.02 ± 3.54 cde	62.86 ± 2.68 abc	53.17 ± 1.93 bc	261.22 ± 81.76 ab
	III	*6*	0.46 ± 0.04 d	0.49 ± 0.15 d	14.09 ± 5.80 cd	65.12 ± 1.49 a	55.16 ± 2.32 ab	294.65 ± 61.04 a
		7	0.45 ± 0.04 d	0.45 ± 0.09 d	18.67 ± 5.25 ab	58.86 ± 2.69 de	51.89 ± 1.17 bc	297.32 ± 44.30 a
		8	0.42 ± 0.02 d	0.25 ± 0.07 e	20.02 ± 7.25 a	60.63 ± 2.23 de	50.52 ± 0.96 c	178.68 ± 29.63 c
		p value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
		HSD	0.04	0.06	3.99	2.72	1.84	71.30
Hot-water blanching	I	0	0.91 ± 0.03 a	0.91 ± 0.01 a	5.75 ± 0.51 c	49.00 ± 1.89 c	56.55 ± 1.98 a	35.74 ± 6.25 d
		1	0.90 ± 0.02 a	0.89 ± 0.01 a	5.35 ± 0.75 c	50.55 ± 2.33 c	56.12 ± 1.66 a	45.27 ± 11.11 d
		2	0.88 ± 0.03 a	0.86 ± 0.02 a	7.13 ± 2.21 c	51.42 ± 1.84 bc	55.00 ± 1.41 a	65.18 ± 17.70 cd
	II	3	0.77 ± 0.03 b	0.63 ± 0.07 b	7.40 ± 1.69 c	59.91 ± 2.72 a	51.86 ± 1.36 b	89.97 ± 24.46 cd
		4	0.70 ± 0.08 c	0.44 ± 0.14 c	15.96 ± 6.14 b	60.13 ± 2.33 a	49.77 ± 2.30 cd	239.58 ± 47.43 b
		5	0.68 ± 0.07 c	0.49 ± 0.08 c	19.55 ± 7.37 b	60.96 ± 2.25 a	50.61 ± 2.01 bc	234.04 ± 78.81 b
	III	*6*	0.50 ± 0.07 d	0.20 ± 0.07 d	35.79 ± 8.08 a	54.82 ± 7.16 b	48.79 ± 1.89 de	292.47 ± 69.77 a
		7	0.49 ± 0.08 d	0.19 ± 0.03 d	31.68 ± 6.09 a	52.63 ± 3.47 bc	47.50 ± 1.38 e	275.45 ± 27.87 ab
		8	0.40 ± 0.02 e	0.17 ± 0.02 d	32.71 ± 8.72 a	54.72 ± 6.27 c	47.66 ± 1.08 e	304.57 ± 31.62 a
		p value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
		HSD	0.05	0.06	5.53	3.83	1.71	42.54

TABLE 3

Treatment	Parameter	Algorithm	Number of features	Wavelengths (nm)	Spectral pre-treatment			LVs[i]	RMSE[l]		Bias		R^2	
					SG[e]	*SC*[f]	*MC*[g]		*C*[m]	*P*[n]	*C*	*P*	*C*	*P*
Control	a_w[a]	PLS[c]	601	1100-2300	9	SNV[h]	Yes	4	0.03	0.04	4.4E-16	-4.7E-04	0.92	0.91
		iPLS[d]	5	1134, 1408, 1724, 2166, 2224				3	0.03	0.03	3.0E-16	-6.2E-05	0.93	0.93
	Moisture (w.b.)	PLS	601	1100-2300	-	SNV	Yes	4	0.04	0.04	4.0E-04	4.0E-04	0.97	0.97
		iPLS	5	1100, 1396, 1558, 1726, 1930				5	0.03	0.03	-1.0E-16	2.6E-05	0.98	0.98
	SSC[b]	PLS	601	1100-2300	7	SNV	Yes	3	3.59	3.68	0.0E+00	1.6E-02	0.63	0.61
		iPLS	8	1108, 1128, 1166, 1320, 1392, 1874, 2088, 2114				6	3.29	3.43	1.2E-13	-3.4E-02	0.69	0.66
	Luminance (L*)	PLS	601	1100-2300	9	SNV	Yes	6	1.55	1.79	0.0E+00	6.2E-03	0.85	0.80
		iPLS	8	1292, 1548, 1778, 1842, 2042, 2160, 2250, 2286				6	1.56	1.66	7.3E-15	-1.1E-02	0.85	0.83
	Carotenoids	PLS	601	1100-2300	9	SNV	Yes	5	27.95	29.51	2.8E-14	-3.0E-02	0.93	0.92
		iPLS	5	1100, 1474, 1868, 2050, 2256				4	27.38	28.17	-1.1E-13	1.2E-01	0.93	0.93
Hot-warter blanching	a_w	PLS	601	1100-2300	7	SNV	Yes	5	0.04	0.04	4.4E-16	-2.8E-04	0.96	0.96
		iPLS	6	1126, 1268, 1400, 1514, 1868, 2300				4	0.04	0.04	-2.7E-17	9.3E-05	0.96	0.96
	Moisture (w.b.)	PLS	601	1100-2300	7	SNV	Yes	5	0.04	0.04	-1.7E-16	-3.9E-04	0.98	0.98
		iPLS	6	1118, 1388, 1588, 1870, 1894, 2216				4	0.04	0.04	-1.8E-16	-2.0E-04	0.99	0.98
	SSC	PLS	601	1100-2300	7	SNV	Yes	3	4.32	4.40	0.0E+00	1.0E-02	0.88	0.88
		iPLS	6	1116, 1278, 1376, 1378, 2098, 2118				4	4.13	4.19	-3.1E-14	1.3E-02	0.89	0.89
	Hue angle (h)	PLS	601	1100-2300	-	SNV	Yes	3	1.40	1.46	-7.1E-15	-1.0E-02	0.86	0.85
		iPLS	8	1316, 1372, 1544, 2186, 2236, 2256, 2270, 2278				6	1.28	1.34	-1.8E-14	5.1E-03	0.88	0.87
	Carotenoids	PLS	601	1100-2300	9	SNV	Yes	6	21.75	23.10	-2.8E-14	-3.4E-01	0.96	0.96
		iPLS	6	1100, 1394, 1754, 1900, 2038, 2236				4	22.17	22.62	2.0E-01	2.4E-01	0.96	0.96

[a] Water activity, [b] Soluble Solids Content, [c] Partial Least Squares regression, [d] Interval Partial Least Squares regression, [e] Savitzky-Golay filter window, [f] Scatter correction algorithm, [g] Standard Normal Variate, [h] Mean Centering, [i] Latent Variables, [l] Root Mean Squared Error, [m] Calibration, [n] Prediction.

TABLE 4

Treatment	Algorithm	Number of features	Wavelengths (nm)	Spectral pre-treatment			LVs[g]	Drying phase (K-means)	Drying time (hours)	Sensitivity		Specificity		Accuracy	
				SG[c]	*SC*[d]	*MC*[f]				*C*[h]	*P*[i]	*C*	*P*	*C*	*P*
Control	PLS-DA[a]	601	1100-2300	9	SNV[e]	Yes	3	I	0-2	0.87	0.86	0.94	0.94	0.91	0.90
								II	3-5	0.91	0.91	0.59	0.59	0.75	0.75
								III	6-8	0.85	0.85	0.87	0.87	0.86	0.86
	iPLS-DA[b]	5	1868, 2152, 2248, 2290, 2294	9	SNV	Yes	5	I	0-2	0.89	0.89	0.96	0.96	0.93	0.92
								II	3-5	0.92	0.91	0.64	0.63	0.78	0.77
								III	6-8	0.90	0.90	0.90	0.90	0.90	0.90
Hot-water blanching	PLS-DA	601	1100-2300	9	SNV	Yes	4	I	0-2	0.96	0.96	0.96	0.96	0.96	0.96
								II	3-5	0.86	0.86	0.89	0.88	0.87	0.87
								III	6-8	0.96	0.96	0.94	0.94	0.95	0.95
	iPLS-DA	6	1376, 1386, 1540, 1980, 2042, 2264	9	SNV	Yes	5	I	0-2	0.97	0.97	0.97	0.97	0.97	0.97
								II	3-5	0.88	0.89	0.91	0.91	0.90	0.90
								III	6-8	0.97	0.97	0.93	0.94	0.95	0.95

[a] Partial Least Squares Discriminant Analysis, [b] Interval Partial Least Squares Discriminant Analysis, [c] Savitzky-Golay filter window, [d] Scatter correction, [e] Standard Normal Variate, [f] Mean Centering, [g] Latent Variables, [h] Calibration, [i] Prediction.

ABSTRACT

The worldwide consumption of dried carrot (*Daucus carota L.*) is on a growing trend. Conventional methods for drying carrots include hot-water blanching followed by hot-air drying, which is usually uncontrolled and therefore prone to product quality deterioration. Thus, there is a need for innovative drying systems that yield high-value end products. In this study, the efficacy of NIR spectroscopy for the non-destructive monitoring of physicochemical changes and drying behaviour in organic carrot slices during 8-h hot-air drying at 40°C was demonstrated using Partial least squares (PLS) regression and PLS Discriminant Analysis (PLS-DA). The impact of hot-water blanching pre-treatment (at 95°C for 1.45 min) for enzyme inactivation on performances of both regression and classification models was also evaluated. PLS regression models were successfully developed to monitor changes in water activity (R^2=0.91-0.96), moisture content (R^2=0.97-0.98), total carotenoids content (R^2=0.92-0.96), lightness for unblanched carrots (R^2 = 0.80-0.83) and hue angle for blanched samples (R^2=0.85-0.87). Soluble solids content prediction was poor for both treatments (RMSEP=3.43-4.40). Classification models were developed to recognise dehydration phases of carrot slices on the basis of their NIR spectral profile using K-means and PLS-DA algorithms in sequence. The performance of each PLS-DA model was defined based on its accuracy, sensitivity and specificity rates. All of the selected models provided from good (>0.85) to excellent (>0.95) sensitivity and specificity for the predefined drying phases. Feature selection procedures yielded both regression and classification models with performances very similar to models computed from the full spectrum.