HIGHLIGHTS

- NIR spectroscopy is a feasible method to control and monitor apple drying
- PLS allows reliable measurement of physicochemical parameters during drying
- PLS-DA allows reliable detection of drying phases of apple wedges
- Microwave treatment affects feature selection for both PLS and PLS-DA models

Real-time monitoring of organic apple (var. *Gala*) during hot-air drying using near-infrared spectroscopy

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ABSTRACT

Dried apple (*Malus domestica* B.) shows a growing trend to its worldwide consumption as raw material to produce organic snacks, integral breakfast foods, chips, etc. Apple is often dried by conventional methods (e.g. hot-air drying, freeze-drying, etc.), which are usually uncontrolled and then prone to product quality deterioration. Thus, there is a need for the development of new drying systems able to guarantee high-value end products. In this study, the feasibility of NIR spectroscopy as smart drying technology to non-destructively detect and monitor physicochemical changes in organic apples wedges during 8-h hot-air drying at 60°C has been investigated. Moreover, the impact of microwave heating pre-treatment (at 850W for 45 sec) as enzyme inactivators on model performances was also evaluated. Partial least squares (PLS) regression models were successfully developed to monitor changes in water activity (R^2 = 0.97÷0.98), moisture content (R^2 = 0.97÷0.98), SSC (R^2 = 0.96÷0.97) and chroma (R^2 = 0.77÷0.86) during drying. Classification analysis was performed for the development of discriminant models able to recognise dehydration phases of apple wedges on the basis of their spectral profile. The classification models were

computed using K-means and Partial Least Squares Discriminant Analysis (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 a very-good (>0.90) or excellent (>0.95) sensitivity and specificity rates for the predefined drying phases. Feature selection procedures allowed to obtain both regression and classification models with performances very similar to models computed from the full spectrum. Results suggest that effect of microwave heating on both water loss and microstructure of apple tissue was pronounced, mainly affecting the features selection procedure in terms of number of features and selected wavelengths.

Keywords: *Malus domestica* B., apple wedges, convective air drying, smart drying, chemometrics, feature selection

1.0 INTRODUCTION

Globalization of market entails the availability of horticultural products regardless of their harvest date, pursued through innovation in products and processes to obtain fruit and vegetables with improved shelf-life, organoleptic quality, nutritional value, safety and healthiness during the whole agrofood chain. Consequently, market value of perishable commodity mainly depends on the preservation method used to guarantee food stability and thus to delay physicochemical, biochemical and microbiological spoilage (Aghbashlo et al., 2015). In fact, the preservation method directly affects processing, storage, transportation and distribution costs.

Among postharvest operations, drying is one of the oldest, typical, effective and viable preservation processes throughout the world. It 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). Drying prevents food spoilage and decay through moisture removal due to simultaneous heat and mass transfer from foods, which may be stored for long periods with minimal deterioration occurring (Nadian et al., 2015). In absence of

sufficient water, microorganisms grow slowly and many of the moisture-mediated reactions, which are responsible for undesirable chemical changes, do not function properly (Mayor and Sereno, 2004; Demirhan and Özbek, 2009). Despite this, drying is not only used to significantly extend shelf-life and nutritional quality of fruit, vegetables, spices and herbs as well as meat and fish, but also to substantially minimize storage and shipping costs (Grabowski et al., 2003). In fact, drying is particularly effective in enabling storability of food at room temperature and simplifying product handling by reducing weight and packaging volume (Liu et al., 2016). Drying technology may vary from simple methods (e.g. sun drying) to relatively advanced techniques (e.g. instant controlled pressure drop drying); nevertheless, modern technology schemes are not always paired with good/excellent quality and high commodity value (Chong et al., 2014; Nadian et al., 2015). In fact, drying is a relatively complex, dynamic, unsteady and nonlinear process that may suffer from properties of wet material, scale of production and compliance with regulations, as well as operating and environmental conditions (Aghbashlo et al., 2015). They may be responsible for quality degradation and result in reduction of consumer acceptance through undesirable changes in colour, texture, size and shape as well as organoleptic, nutritional and functional properties (Brosnan and Sun, 2004; Vega-Gálvez et al., 2012). Last but not least, drying is one of the most energy-intensive processes in food industry (Akpinar et al., 2003); in fact, it adversely effects climate change as most dryers use fossil fuels (Mujumdar, 2012). Consequently, with the aim of circumventing the aforementioned issues, new drying technologies must be designed around the quality attributes of the raw material to ensure valuable products at the highest drying rate and the lowest carbon footprint, which means minimal/optimal energy demand and negligible environmental impact (Mujumdar, 2012; Su et al., 2015). Among emerging drying technologies, smart drying is one of the newest and most promising techniques. It has potential to guarantee high-value end products, while enhancing drying efficiency, by implementing innovative and reliable sensors, resources, tools and practices. Moreover, smart drying can be cost-effective in both real-time monitoring of foodstuffs quality and dynamic controlling of operating conditions along the whole 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), visible (Vis) and near-infrared (NIR) spectroscopy (Nicolaï et al., 2007), 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 system for the drying environment.

Among commercial fruits, apple shows a growing trend to its worldwide consumption (Rodríguez et al., 2014), where dried apple plays a major role in food industry as raw material for the production of snacks, integral breakfast foods, chips, etc., which have become popular in the diet of modern consumers (Vega-Gálvez et al., 2012; Yi et al., 2015) in parallel with the human consumption of organic products (Sacilik and Elicin, 2006). Despite apple tissue exhibits extensive and not homogeneous discoloration during drying (Fernández et al., 2005), it is nowadays often dried by conventional methods (e.g. hot-air drying, freeze-drying, etc.) which, however, are usually uncontrolled and then prone to product quality deterioration as well as the fact of being affected by a number of drawbacks, such as very long drying time and, of course, high energy demand (Chong et al., 2014; Nadian et al., 2015). Thus, treatment selection before apple drying is a mandatory (but not sufficient) step to obtain a high-value end product. However, because not all conventional drying treatments are allowed by the European Organic Regulation on production and labelling of organic products (i.e. EC No. 834/2007 and EC No. 889/2008), drying of organic apples should be carefully optimized to obtain comparable results to conventional methods.

Therefore, the main objective of the proposed study was to investigate the feasibility of near-infrared (NIR) spectroscopy as smart drying technology to proactively and non-destructively detect and monitor quality change in organic apple wedges during hot-air drying. Based on authors' best knowledge, apple drying has been widely addressed in literature; nevertheless, little insight is available on smart drying of apples, while knowledge of its potential use in the organic sector is

105 totally lacking. NIR spectroscopy was investigated as proved on-/in-line tool with high sensitivity
106 to changes in moisture content, particle size and chemical state of food (Ozaki et al., 2006).

107 **2.0 MATERIALS AND METHODS**

108 *2.1 Sample preparation*

109 Organic apples (*Malus domestica* B. var. Gala) were purchased from a local organic trader
110 (Biobox srl, Viterbo, Italy) and immediately stored at 4 ± 1 °C until processing. Fruit sampling was
111 performed by selecting sound apples, with uniform size and same ripening stage. Fruits were
112 tempered to room temperature 15 h before starting the experimental activities.

113 Apple wedges, without core and peel, were prepared by washing and cutting fruit into discs
114 (5-mm thick) and subsequently dividing each disc into quarters using a cork borer and a sharp
115 ceramic knife. Samples were visually evaluated for quality assessment and only apple wedges free
116 from decay and/or blemish were used in the experimentation to perform (1) hot-water blanching and
117 microwave heating treatments and (2) hot-air drying tests.

118 About 100 g of apple wedges were used for both hot-water and microwave treatment
119 experiments, while 270 apple wedges were randomly arranged into 9 batches of 30 samples each for
120 the use in drying experiment. Fruit wedges were subjected to 8-h hot-air drying and batch sampling
121 was performed at 0, 1, 2, 3, 4, 5, 6, 7 and 8 h drying. Each batch was subjected to both NIR spectral
122 data acquisition and determination of CIELab color, moisture content, water activity (a_w) and
123 soluble solids content.

124 *2.2 Treatment before hot-air dehydration*

125 *2.2.1 Hot-water blanching*

126 Hot-water blanching consisted of dipping apple wedges in hot-water with a temperature
127 controlled water bath (Astor 800D, Astori Tecnica, Brescia, Italy). As a control, apple wedges were
128 dipped in distilled water at room temperature. The experimental plan is reported in Table 1. Treated
129 samples were immediately cooled for 3 min in ice-water, and the residual POD enzymatic activity
130 was evaluated.

2.2.2 Microwave heating

A turntable domestic microwave oven (MT243, Whirlpool Co., Michigan, United States) with a continuous output-power (2450 MHz, 1000 W) was used to treat apple wedges. An experimental design based on a factorial design was applied (Table 1). Powers and times of treatment were chosen by taking into consideration the results of preliminary experiments aimed at identifying proper process conditions to allow apple wedges to be uniformly treated. After treatment, apple wedges were removed from the microwave oven and immediately dipped in ice-water for 3 min to accelerate cooling. Residual POD activity was then evaluated.

2.3 Peroxidase activity

2.3.1 Enzyme purification

Enzyme purification was carried out on the basis of the method of Massantini et al. (2009) with some modifications. Apple wedges were collected after each blanching treatment, frozen with liquid nitrogen and then immediately grinded into frozen powder by an analytic mill (IKA A11 basic; IKA Labortechnik, Staufen, Germany). Three grams of apple 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

Peroxidase (POD) activity was measured by 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

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

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 coefficient of determination (R^2) of each regression line was also computed.

A POD inactivation of 90% was fixed as 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 in 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 apple wedge. The dehydration process was conducted at 60°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 lower than 60°C were discarded due samples developing browning within the first 2 hours of dehydration.

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. (2013a). Each sample was measured in duplicate on two opposite sides of each apple wedge (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 apple wedge 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 Chemometrics

2.5.3.1 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 some linear combinations of the original independent variables. By using these linear combinations alone, PLS allowing the discarding of irrelevant and unstable information, solving collinearity problem and, finally, obtaining a more stable regression equation. In addition, the Interval PLS (iPLS) algorithm was also used to select a subset of wavelengths which could describe superior prediction compared

206 to PLS models based on all features dataset (Xing et al., 2008). The iPLS algorithm was configured
207 in stepwise forward mode for the selection of a maximum of 10 wavelengths.

208 As PLS and iPLS regressions perform a dimensionality reduction, it is essential to test each
209 model and select the correct number of latent variables to find the optimal trade-off between under-
210 fitting and over-fitting. Thus, the samples were randomly split as follows: 75% and 25% of the
211 samples were assigned to the calibration set (C) and the prediction set (P), respectively. Every PLS
212 and iPLS model was optimized by computing a venetian blinds cross-validation with 10 data splits.
213 This cross-validation method was preferred because it is simple and easy to implement, relatively
214 fast, generally safe and capable of providing a better representation when the dataset contains many
215 samples, as is the case here (Naes et al., 2004; Wise, 2009). Root Mean Squared Error for
216 calibration, cross-validation and prediction calculations (RMSEC, RMSECV and RMSEP,
217 respectively) were employed to evaluate each regression model with the purpose of selecting the
218 optimal number of latent variables and thus circumvent unrealistic results (Moscetti et al., 2015).
219 Model performances were also evaluated in terms of BIAS and coefficient of determination (R^2).

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

222 *2.5.3.2 Prediction of the drying phases (classification models development)*

223 Classification models were developed using K-means and Partial Least Squares
224 Discriminant Analysis (PLS-DA) algorithms in sequence (Fig. 1). As initial step, K-means was
225 employed to determine the number of drying phases (i.e. classes) and to label each sample as
226 belonging to a specific class on the basis of the observed changes in moisture content, water
227 activity, CIELab color and soluble solids content. K-means is a partitional clustering method
228 belonging to the group of the unsupervised hierarchical cluster analyses. The selection of the most
229 appropriate cluster solution was performed by computing both actual and random sum of squared
230 errors (SSE) for a maximum of 9 clusters (i.e. 9 times of dehydration). Random SSEs were
231 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 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 apple wedge 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 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). In detail, 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) $$Accuracy\ rate = \frac{True\ Positives + True\ Negatives}{Total\ Positives + Total\ Negatives}$$

Similarly to what already 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.

Colour of apple wedge was measured with a spectrophotometer (CM-2600d, Konica Minolta, Osaka, Japan). The mode used for acquiring data was CIE Standard Illuminant D65 (Daylight), Observer 10° and 6-mm diameter of measurement aperture. Four replications were performed for each sample by performing two colour measurements on two opposite sides of each apple wedge. 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., 2013a).

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).

2.7 Statistical analysis 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 standard error 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 in the tables and figures were back transformed.

Data handling and ANOVA were both performed using R v3.2.4 software in combination with 'agricolae' v1.2-3 R-package (CRAN, 2016). 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 research work, the apple drying process was monitored using NIR spectroscopy. NIR-based regression and classification models were computed and the impact of thermal treatments as enzyme inactivators on model performances was also investigated.

3.1 Thermal treatment selection

The effect of thermal treatments on apple wedges was evaluated for both hot-water blanching and microwave heating treatments at pre-established range of temperature and power, respectively (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 gives reasonable assumption that other quality-deteriorative enzymes (e.g. pectinmethylesterase, polyphenol oxidase, etc.) are also inactivated.

Inactivation kinetics were determined through semi-log plot of residual POD activity versus time. Results showed excellent linear fits (R^2 = 0.93÷0.99) at all temperatures/powers 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 with microwave heating (Fig. 2b). In fact, hot-water blanching was less effective, showing slowest inactivation rate constants (k) (0.17, 0.46 and 0.79 min^{-1} at 80, 90 and 95°C, respectively) in comparison with microwave heating (1.08, 1.81 and 3.03 min^{-1} at 350, 650 and 850 W, respectively). Moreover, microwave treatment led to better colour retention in apple wedges than hot-water blanching (data not shown). Although the mechanism is still unclear and several controversial opinions must be faced (Awuah et al., 2007), similar results were reported by several authors (Awuah et al., 2007; Matsui et al., 2008; Zheng and Lu, 2011; Latorre et al., 2012; Rattanadecho and Makul, 2016). It seems that microwave irradiation may be more effective and faster for facing enzyme inactivation when compared with conventional methods, because of concurrent thermal (i.e. heat denaturation of protein) and non-thermal (i.e. microwaves interaction

with polar and/or charged moieties of protein) effects of microwaves (Olsen et al., 1966; Kermasha et al., 1993; Matsui et al., 2008; Rattanadecho and Makul, 2016).

Finally, the lowest decimal reduction time (*D*) among treatments was achieved by using microwave at 850 W for 0.77 min (~ 46.2 sec) of irradiation. Thus, considering that the evaluation of the effects of thermal treatment on nutritional value of product was not part of the present study, microwave heating at 850 W for 45 sec was selected as the most adequate treatment to obtain colour-stable apple wedges 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 microwave heating treatments, respectively) and among drying times. Specifically, changes in the spectral profiles during the drying process were evident to the naked eye for the control treatment only. 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, starch and proteins (Ambrose et al., 2016). On the other hand, microwave-heated samples apparently showed less changes in spectral shape during the drying process and less pronounced shoulders on either side of the two principal water absorption bands (1450 and 1940 nm). Results allow to speculate that those differences in spectral profile should be mainly due to both water loss and changes in forward scattering and backscattering by flesh tissue as consequence of the microwave heating treatment.

3.3 Chemical and physicochemical changes

Table 2 summarizes changes in chemical and physicochemical parameters on treated (i.e. microwave heated) and untreated (i.e. control) apple wedges 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 SSC increased due to decline in water content. Results were perfectly in agreement with those of other authors (Romano et al., 2011; Dénes et al., 2012). However, different drying behaviours between treatments were noted. In fact, microwave-treated samples showed a faster decrease in water activity during drying and a higher experimental variability for SSC, probably due to the higher heterogeneity of the raw material. The data also pointed that colour of treated apple wedges was totally different from the untreated one. Microwave heating entailed less colour changes during drying and it was responsible for lower initial (0-h drying) and final (8-h drying) CIELab values of lightness (L^*), redness (a^*) and yellowness (b^*) of product. Although microwave heating better retained the colour due to reduction in enzymatic browning, colour changes during drying showed a similar trend between treatments, probably due to Maillard reaction occurrence. In general, the variation in L^* value was unclear and practically independent of thermal treatment, similarly to the results obtained by Krokida et al. (1998, 2001); while drying time was found to increase redness (a^*), yellowness (b^*) and chroma (C^*) and to decrease hue-angle (h).

The chemical and physicochemical features of 270 apple wedges per treatment were clustered using the K-means algorithm. A cluster analysis was performed in each treatment group. On the basis of the scree plots obtained for the difference between the actual and random SSEs against the cluster solutions (data not shown), the optimal cluster level was identified as three and thus samples were split into three main classes, each characterized by a specific drying period (also named ‘Drying phase I’, ‘Drying phase II’ and ‘Drying phase III’) (Table 2). Results showed that the duration of drying phases slightly differed between treatments. In fact, the control treatment showed a shorter ‘Drying phase II’ (i.e. from 3 to 4 hours of drying) in comparison with the microwave heating treatment (i.e. from 3 to 5 hours 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.

364

365

366 *3.3 Regression models*

367 The complete calibration and prediction performances of the regression models are
368 summarized in Table 3. PLS regression models with good or excellent predictability were obtained
369 to monitor changes in a_w (Fig. 3a), moisture content (Fig. 3b), chroma (Fig. 3c) and SSC (Fig. 3d)
370 of apples wedges during drying, regardless both thermal treatment and number of features used in
371 the model. In detail, except for calibration model for chroma, the coefficient of determination (R^2)
372 was higher than 0.96 for all the aforementioned quality parameters. Thus, for the test set validation
373 with one quarter of the data (randomly selected) RMSEPs ranging from 0.03÷0.04 for a_w, 0.04÷0.05
374 for moisture content and 4.54÷4.99 for SSC were obtained. The latter performance parameter was
375 comparable with both calibration and cross-validation results. Moreover, the model obtained from
376 feature selection (i.e. iPLS model) usually allowed the use of a lower number of latent variables in
377 comparison with full-spectrum model (i.e. PLS model).

378 The model for chroma determination resulted in lower R^2 but still in good performance. In
379 fact, although the correlation was smaller (R^2 from 0.77 to 0.86), the model performance was
380 acceptable, showing a RMSEP ranging from 2.31 to 2.75. Considering that the 1100-2300-nm
381 spectral band is not directly related to colour information, results obtained by the indirect
382 measurement of changes in chroma can be considered very good. However, it can be speculated that
383 by including the visible range the model performance could be improved considerably.

384 Generally, with respect to the treatment, iPLS algorithm led to a higher number of selected
385 features for microwave-heated samples, which also differed from the control treatment in terms of
386 selected wavelengths. Results suggest that effect of microwave heating on water loss and changes in
387 microstructure was pronounced, affecting the model development.

388 Table 3 also gives an overview of the spectral pre-treatments effectively used in the selected
389 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 to obtain the highest R^2. This may either mean that the variation in light scattering negatively interfered with spectral information related to chemical and physicochemical parameters. Savitzky-Golay smoothing filter improved the prediction performance for all regression challenges. Thus, the need for a smoothing filter suggests that spectral data were slightly affected by issues due to noise and other irrelevant information. 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.

3.4 Classification models

In Table 4 are summarized the combinations of spectral pre-treatments, discriminant algorithms and features which gave the best classification performance for the assignment of each apple wedge to a specific drying phase on the basis of its spectral profile. The optimal combination of spectral pre-processing was similar of those already selected for the development regression models. Thus, in this case also, 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).

Considering the large variability observed in samples during drying, models show very high classification performances. In fact, all the models possessed very-good (> 0.90) or excellent (> 0.95) sensitivity and specificity rates for all drying phases (i.e. ‘Drying Phase I’, ‘Drying Phase II’ and ‘Drying Phase III’). This means that the models had a greater ability to discriminate between the classes with respect to another class. In particular, all models had the highest sensitivity rate and specificity rate for ‘Drying Phase I’ and ‘Drying Phase III’. This indicates that the classification of apple wedges 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 'Drying phase II' showed (1) a lower within-class similarity and (2) a higher between-class similarity than both 'Drying Phase I' or 'Drying Phase III'.

Feature selection demonstrated that development of a drying-phase recognition model based on few wavelengths is feasible. In particular, 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. This is confirmed by both Fig. 5a and 5b, which show an example of tight pattern similarity between scores from PLS-DA and iPLS-DA models. Finally, yet importantly, the experimentation showed a negligible effect of microwave heating treatment on the performances of both PLS-DA and iPLS-DA models. However, feature selection seems to be affected by the thermal treatment as selected wavelengths were totally 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 apples due to the effect of both 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 has been evaluated to proactively and non-destructively detect and monitor changes in quality parameters (i.e. water activity, moisture content, SSC and colour) of apple wedges (*Malus domestica* B. var. Gala) during hot-air drying. For this purpose, both PLS regression and PLS-DA classification models were developed. Optimal features were selected by using the interval PLS (iPLS) and the interval PLS-DA (iPLS-DA) algorithms both configured in stepwise forward mode. The impact of the microwave heating (at 850 W for 45 sec) as enzyme inactivator on model performance was also investigated.

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 = 0.97÷0.98; RMSEP = 0.03÷0.04), moisture content (R^2 = 0.97÷0.98; RMSEP = 0.04÷0.05), SSC (R^2 = 0.96÷0.97; RMSEP = 4.54÷4.99) and chroma (R^2 = 0.77÷0.86; RMSEP = 2.31÷2.75). Regarding the discriminant analysis, PLS-DA algorithms obtained high accuracy rate in classifying the apple wedges into classes as drying phases based on the spectral profile. Specifically, NIR spectroscopy showed an excellent classification (accuracy rate > 0.95) for apple wedges belonging to 'Drying phase I' and 'Drying phase II'. Differently, misclassified apple wedges were primarily assigned to 'Drying phase II', which however showed a very-good accuracy rate higher than 0.90. It should be noted that the development of regression and classification models were affected by the microwave heating treatment in terms of number of features and selected wavelengths. Consequently, the proposed method should be further validated to circumvent model robustness issues due to both water loss and microstructural changes in apples as consequence of thermal treatments.

Finally, the approach proposed in this research lays the foundations 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 be conditional of the spectral pre-treatment used. Future research should include testing wavelengths not measured 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.

5.0 ACKNOWLEDGMENTS

The authors gratefully acknowledge CORE Organic Plus consortium (Coordination of European Transnational Research in Organic Food and Farming System, ERA-NET action) and Mipaaf (Ministero delle politiche agricole alimentari e forestali - Italy) for financial support through

the SusOrganic project titled: ‘Development of quality standards and optimized processing methods for organic produce’. Moreover, our sincere thanks to the master student Mirko Grilli for his valuable help and support during the experimentation.

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615

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, color 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. *First-order kinetics of the residual peroxidase activity for control (a) and microwaves (b) treatments. D-value states for decimal reduction time, which is the treatment time required to reduce the residual POD activity to at least 0.1.*

Figure 3. *Mean relative absorbance spectra for control (a) and microwave heating (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), chroma (column c) soluble solids content (column d) monitored during 8-h drying in both control (row 1) and microwave (row 2) treated apples. 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', '3-4 h' and '5-8 h' classes (i.e. drying phases) of the control treatment. Percentages of the explained variance are reported in parentheses on the axes. Green point with red outline corresponds to 'Drying Phase II' sample misclassified as 'Drying Phase I'. Red point with green outline corresponds to 'Drying Phase I' sample misclassified as 'Drying Phase II'. Blue point with green outline corresponds to 'Drying Phase III' sample misclassified as 'Drying Phase II'. Green point with blue outline corresponds to 'Drying Phase II' sample misclassified as 'Drying Phase III'.*

Figure 1

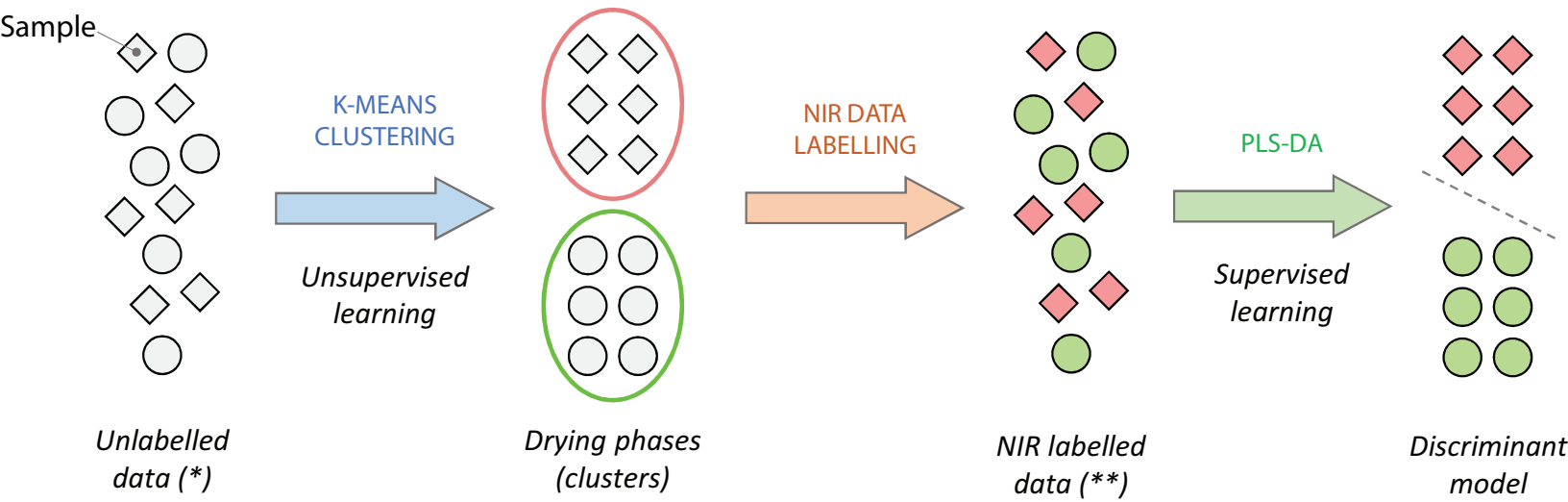

Sample
K-MEANS CLUSTERING
Unsupervised learning
NIR DATA LABELLING
PLS-DA
Supervised learning
Unlabelled data (*)
Drying phases (clusters)
NIR labelled data (**)
Discriminant model

Figure 2

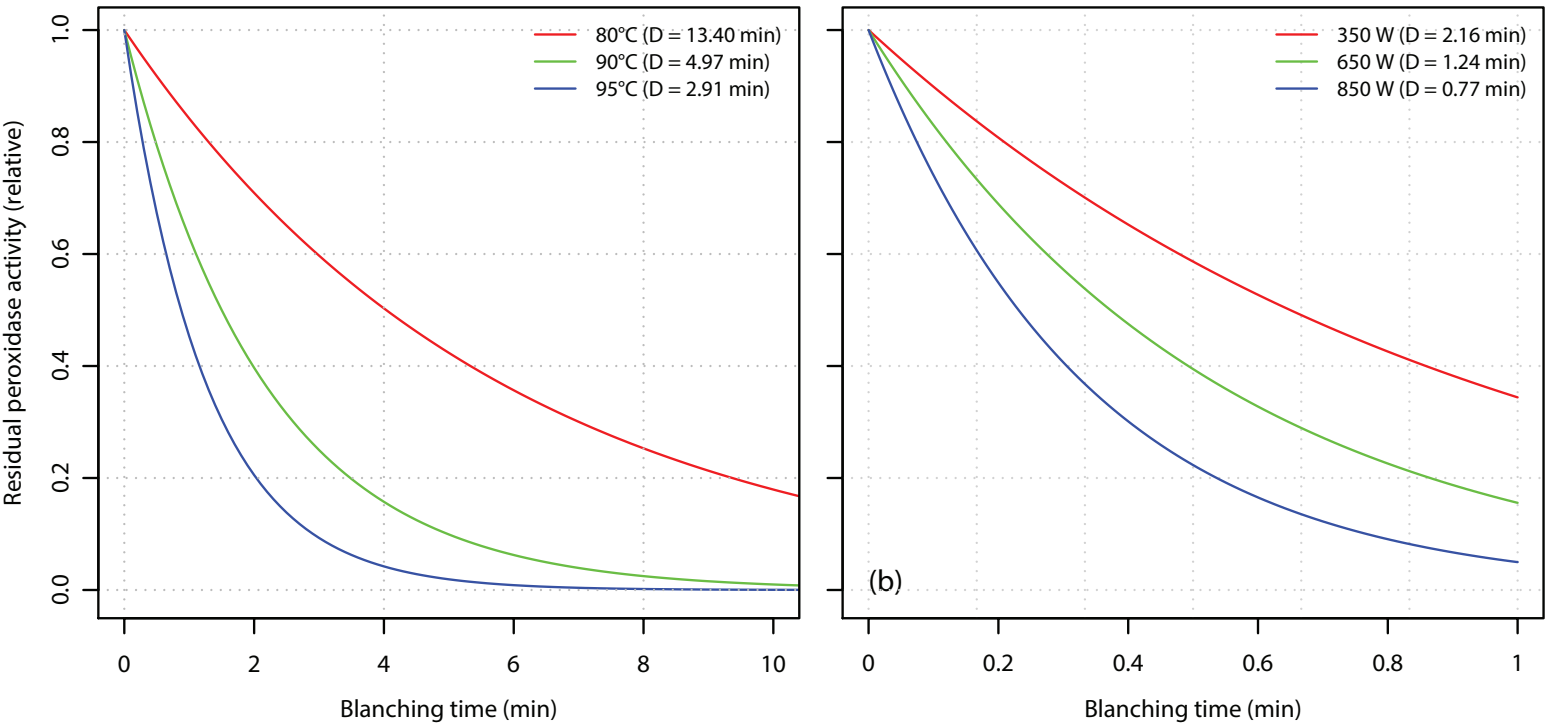

Residual peroxidase activity (relative)
0.0
0.2
0.4
0.6
0.8
1.0
80°C (D = 13.40 min)
90°C (D = 4.97 min)
95°C (D = 2.91 min)
0
2
4
6
8
10
Blanching time (min)
(b)
350 W (D = 2.16 min)
650 W (D = 1.24 min)
850 W (D = 0.77 min)
0
0.2
0.4
0.6
0.8
1
Blanching time (min)

Figure 3

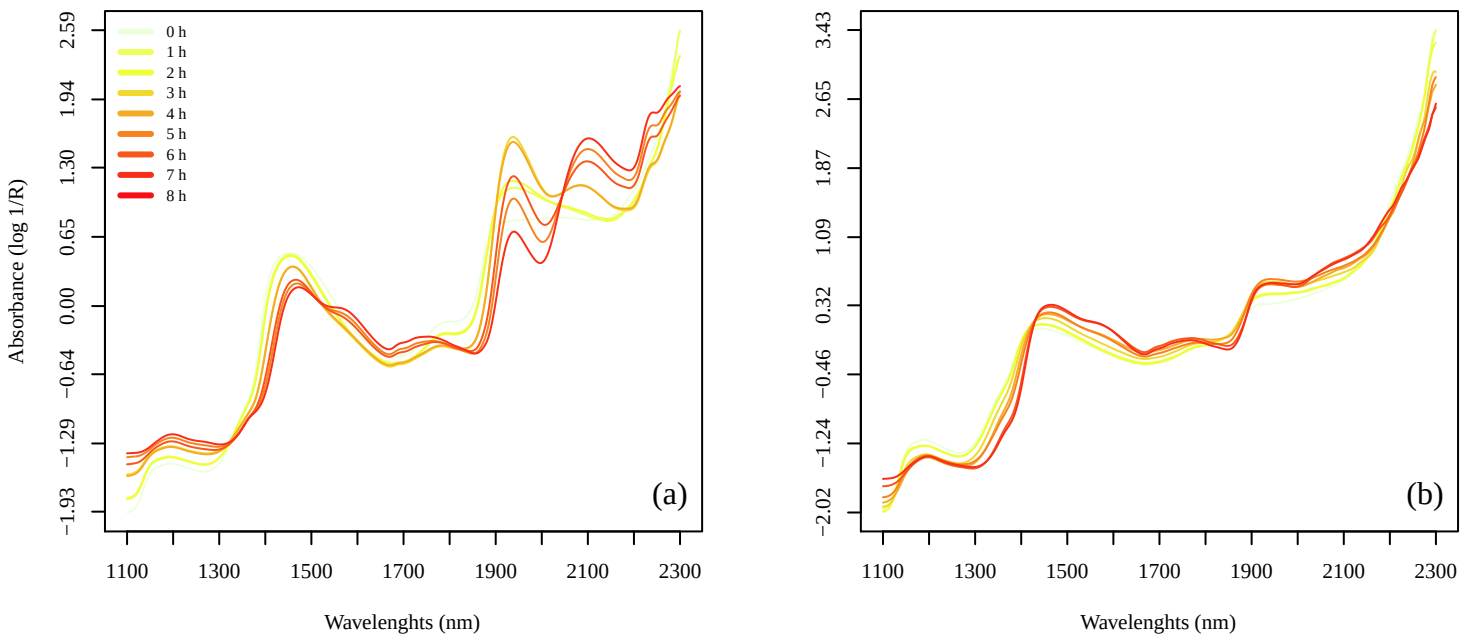

0 h
1 h
2 h
3 h
4 h
5 h
6 h
7 h
8 h
Absorbance (log 1/R)
−1.93
−1.29
−0.64
0.00
0.65
1.30
1.94
2.59
1100
1300
1500
1700
1900
2100
2300
Wavelenghts (nm)
(a)
−2.02
−1.24
−0.46
0.32
1.09
1.87
2.65
3.43
1100
1300
1500
1700
1900
2100
2300
Wavelenghts (nm)
(b)

Figure 4

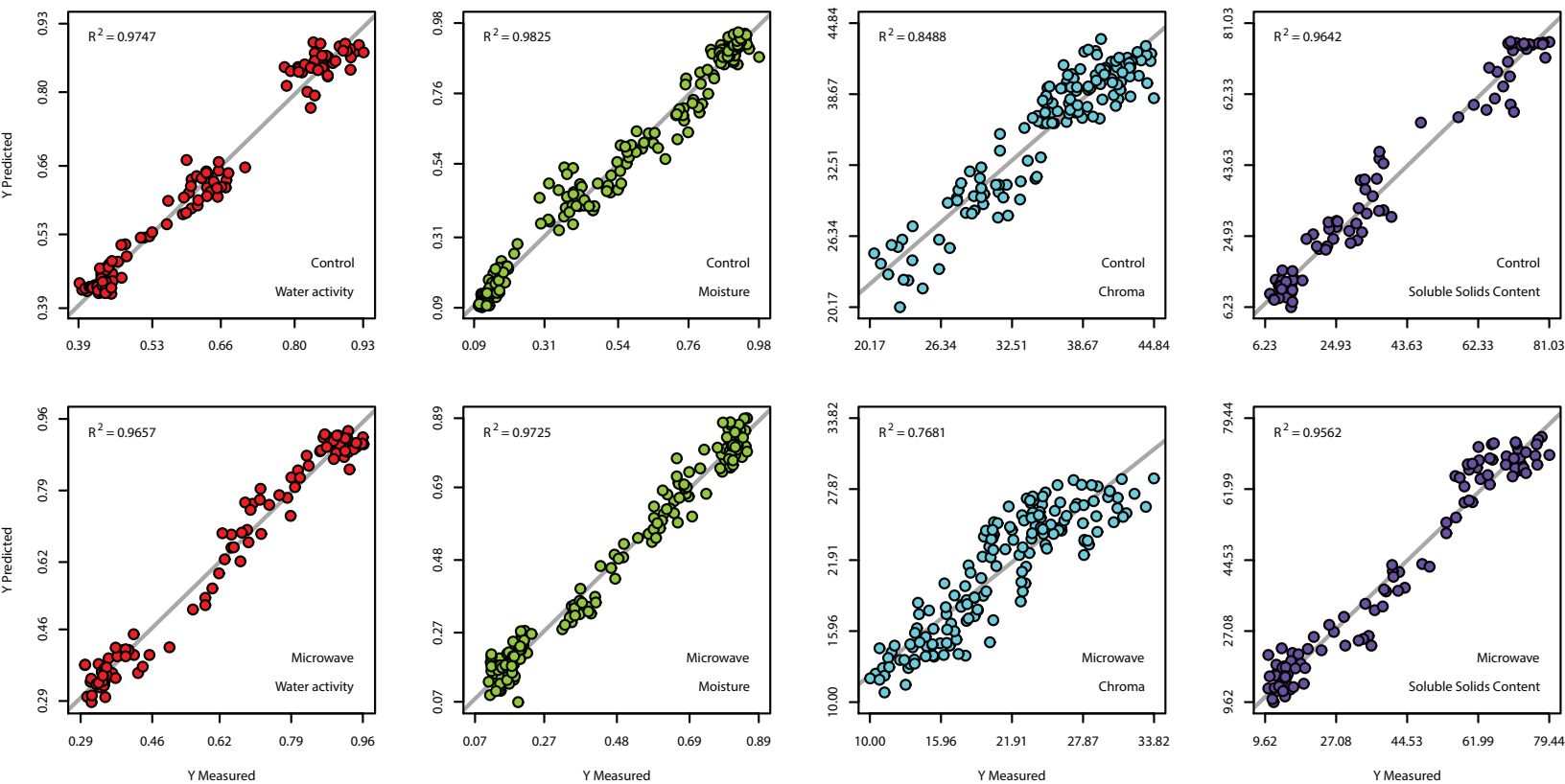
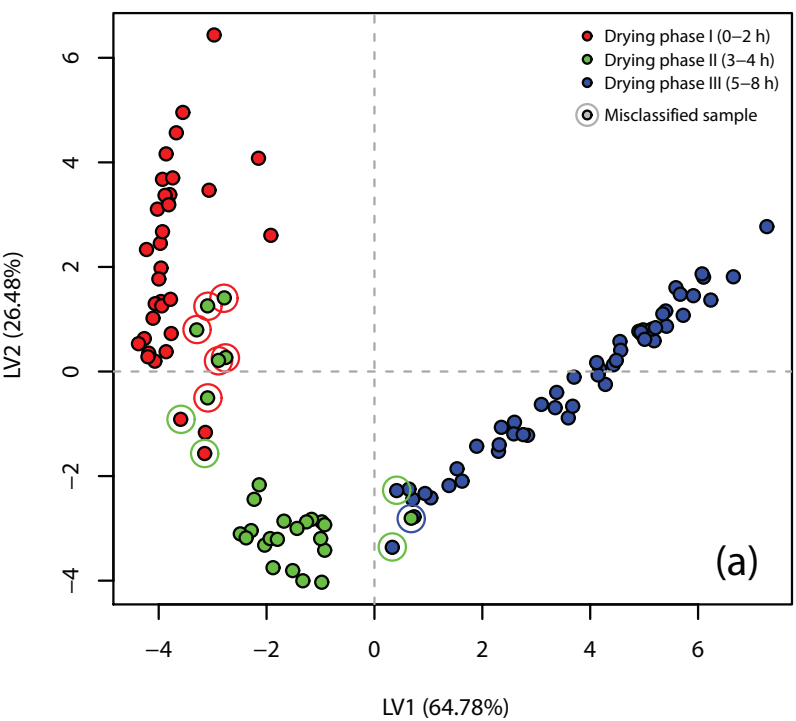

R² = 0.9747
Control
Water activity
R² = 0.9825
Control
Moisture
R² = 0.8488
Control
Chroma
R² = 0.9642
Control
Soluble Solids Content
R² = 0.9657
Microwave
Water activity
R² = 0.9725
Microwave
Moisture
R² = 0.7681
Microwave
Chroma
R² = 0.9562
Microwave
Soluble Solids Content
Y Predicted
Y Measured

Figure 5


Drying phase I (0–2 h)
Drying phase II (3–4 h)
Drying phase III (5–8 h)
Misclassified sample
(a)
LV1 (64.78%)
LV2 (26.48%)
−4
−2
0
2
4
6

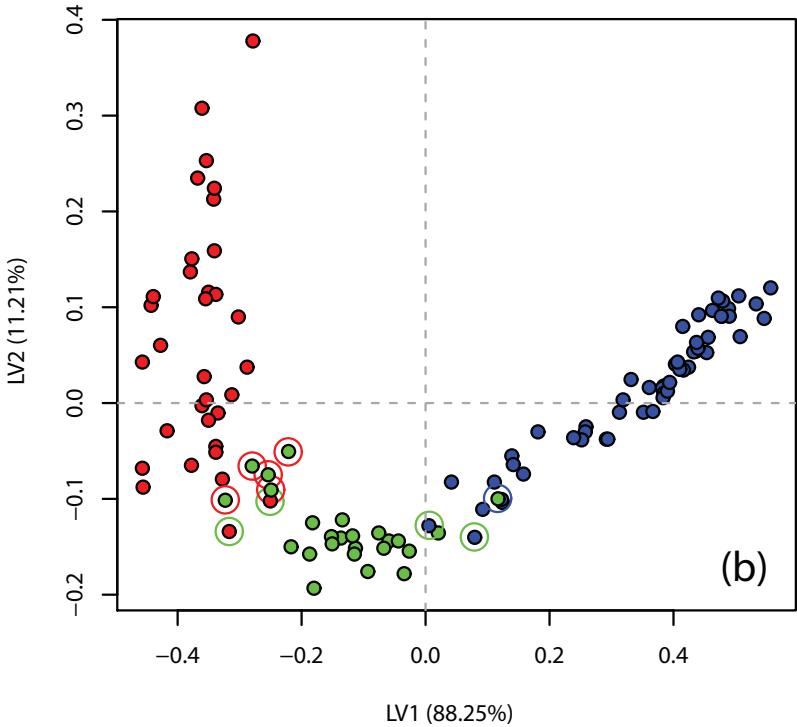

(b)
LV1 (88.25%)
LV2 (11.21%)
−0.4
−0.2
0.0
0.2
0.4
−0.2
−0.1
0.0
0.1
0.2
0.3
0.4

TABLE CAPTIONS

Table 1. *Experimental design for both hot-water and microwave blanching treatments. HW – hot-water blanching; MW – microwave heating.*

Table 2. *Main effect of drying time on the chemical and physicochemical quality parameters of apple wedges. 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

Hot-water blanching			Microwave heating		
ID	**Temp. (°C)**	**Time (min)**	**ID**	**Power (W)**	**Time (min)**
HW-80-0	80	0.0	MW-350-0	350	0.00
HW-80-1	80	1.5	MW-350-1	350	0.25
HW-80-2	80	3.0	MW-350-2	350	0.55
HW-80-3	80	5.0	MW-350-3	350	0.75
HW-80-4	80	10.0	MW-350-4	350	1.00
HW-90-0	90	0.0	MW-650-0	650	0.00
HW-90-1	90	1.5	MW-650-1	650	0.25
HW-90-2	90	3.0	MW-650-2	650	0.50
HW-90-3	90	5.0	MW-650-3	650	0.75
HW-95-0	95	0.0	MW-650-4	650	1.00
HW-95-1	95	0.5	MW-850-0	850	0.00
HW-95-2	95	1.0	MW-850-1	850	0.25
HW-95-3	95	1.5	MW-850-2	850	0.50
HW-95-4	95	3.0	MW-850-3	850	0.75
			MW-850-4	850	1.00

Table 2

TABLE 2

Treatment	Drying phase (K-means)	Drying time (hour)	Water activity (a_w)	Moisture (relative)	SSC (°Brix)	Lightness (*L**)	Redness (*a**)	Yellowness (*b**)	Hue angle (*h*)	Chroma (*C**)
Control	I	0	0.88 ± 0.04 a	0.89 ± 0.00 a	11.39 ± 1.43 e	71.66 ± 1.65 d	2.92 ± 0.96 c	23.30 ± 1.83 g	82.93 ± 1.97 a	23.49 ± 1.89 f
		1	0.84 ± 0.04 ab	0.85 ± 0.02 a	13.01 ± 0.35 e	71.23 ± 2.53 de	5.01 ± 0.73 b	28.71 ± 1.33 f	80.13 ± 1.02 bc	29.14 ± 1.42 e
		2	0.82 ± 0.05 b	0.83 ± 0.03 a	14.74 ± 0.52 e	68.89 ± 1.56 d	6.06 ± 0.80 b	31.59 ± 1.76 e	79.17 ± 0.99 bcd	32.17 ± 1.85 d
	II	3	0.64 ± 0.03 c	0.58 ± 0.09 b	24.85 ± 1.96 d	75.20 ± 2.38 bc	8.16 ± 1.24 a	37.67 ± 2.76 bcd	77.79 ± 1.44 de	38.56 ± 2.86 bc
		4	0.62 ± 0.03 c	0.50 ± 0.09 c	35.77 ± 4.40 c	76.65 ± 1.84 ab	6.17 ± 1.05 b	36.07 ± 2.55 d	80.34 ± 1.23 bc	36.60 ± 2.65 c
	III	*5*	0.45 ± 0.03 d	0.16 ± 0.06 e	38.85 ± 2.29 c	78.46 ± 2.69 ab	6.46 ± 2.00 b	39.28 ± 2.44 abc	80.75 ± 2.35 b	39.84 ± 2.67 ab
		6	0.46 ± 0.04 d	0.25 ± 0.11 d	58.50 ± 4.93 b	76.22 ± 2.85 ab	8.34 ± 2.03 a	40.48 ± 2.49 a	78.43 ± 2.50 cde	41.37 ± 2.67 ab
		7	0.45 ± 0.04 d	0.10 ± 0.04 ef	69.11 ± 5.42 a	73.13 ± 1.89 cd	8.89 ± 1.19 a	37.49 ± 2.65 cd	76.63 ± 1.73 e	38.55 ± 2.65 bc
		8	0.42 ± 0.02 d	0.10 ± 0.04 f	75.48 ± 2.64 a	73.25 ± 3.27 cd	9.03 ± 1.76 a	40.07 ± 1.67 ab	77.33 ± 2.30 de	41.11 ± 1.78 ab
		p value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
		HSD	0.04	0.06	7.59	2.72	1.60	2.56	2.09	2.68
Microwave heating	I	0	0.91 ± 0.03 a	0.87 ± 0.02 a	11.97 ± 1.15 d	44.21 ± 2.59 abc	-2.07 ± 0.45 c	13.61 ± 2.25 d	98.70 ± 1.46 ab	13.77 ± 2.27 d
		1	0.92 ± 0.02 a	0.83 ± 0.02 ab	15.20 ± 1.21 d	42.05 ± 1.46 bcd	-2.03 ± 0.75 c	13.19 ± 2.54 d	99.35 ± 4.40 a	13.38 ± 2.45 d
		2	0.88 ± 0.04 a	0.81 ± 0.02 b	16.84 ± 3.36 d	45.46 ± 1.86 ab	-1.48 ± 0.59 c	16.32 ± 2.54 cd	95.31 ± 2.14 bc	16.40 ± 2.53 cd
	II	3	0.75 ± 0.07 b	0.62 ± 0.04 c	34.25 ± 11.43 c	46.44 ± 1.16 a	-1.52 ± 0.70 c	19.28 ± 2.22 c	94.72 ± 2.34 c	19.35 ± 2.18 c
		4	0.60 ± 0.12 c	0.42 ± 0.09 d	46.75 ± 9.74 b	43.29 ± 3.98 abcd	0.54 ± 1.86 b	25.08 ± 3.95 ab	89.17 ± 3.92 d	25.14 ± 4.00 ab
		5	0.58 ± 0.11 c	0.36 ± 0.06 e	48.63 ± 12.31 b	44.44 ± 3.84 ab	1.23 ± 1.90 b	27.23 ± 3.56 a	87.80 ± 3.63 d	27.31 ± 3.64 a
	III	*6*	0.36 ± 0.02 d	0.19 ± 0.01 f	73.21 ± 13.23 a	40.46 ± 1.70 d	0.98 ± 0.90 b	24.64 ± 2.85 ab	87.87 ± 2.00 d	24.68 ± 2.87 ab
		7	0.35 ± 0.02 d	0.18 ± 0.02 f	63.49 ± 6.14 a	40.85 ± 2.83 cd	0.79 ± 2.03 b	22.95 ± 2.37 b	88.28 ± 4.64 d	23.04 ± 2.45 b
		8	0.32 ± 0.02 d	0.19 ± 0.03 f	73.22 ± 3.80 a	43.49 ± 7.86 abcd	3.87 ± 3.32 a	25.75 ± 6.21 ab	82.19 ± 5.37 e	26.15 ± 6.58 ab
		p value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
		HSD	0.08	0.04	10.73	3.58	1.64	3.37	3.54	3.46

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	5	SNV[h]	Yes	4	0.03	0.03	2.2E-16	-5.7E-05	0.98	0.97
		iPLS[d]	6	1144, 1496, 1876, 2118, 2166, 2290				4	0.02	0.03	-3.5E-16	9.1E-05	0.98	0.98
	Moisture	PLS	601	1100-2300	5	SNV	Yes	5	0.04	0.04	1.1E-16	-4.2E-04	0.98	0.98
		iPLS	2	1330, 1878				2	0.04	0.04	-3.1E-16	-1.3E-04	0.98	0.98
	SSC[b]	PLS	601	1100-2300	9	SNV	Yes	5	4.48	4.86	0.00E+00	6.07E-03	0.97	0.96
		iPLS	2	1310, 1878				2	4.61	4.63	4.49E-14	1.09E-02	0.97	0.97
	Chroma (C*)	PLS	601	1100-2300	15	SNV	Yes	6	2.23	2.43	-7.1E-15	-1.5E-02	0.87	0.85
		iPLS	4	1156, 1630, 2180, 2244				4	2.25	2.33	1.8E-14	-1.3E-02	0.87	0.86
Microwave heating	a_w	PLS	601	1100-2300	9	SNV	Yes	6	0.04	0.04	0.0E+00	-7.2E-05	0.98	0.97
		iPLS	8	1340, 1444, 1534, 1652, 1658, 1768, 1868, 1888				4	0.04	0.04	5.4E-17	3.0E-04	0.98	0.97
	Moisture	PLS	601	1100-2300	7	SNV	Yes	8	0.04	0.05	-1.1E-16	-1.4E-03	0.98	0.97
		iPLS	7	1140, 1354, 1424, 1438, 1876, 1892, 2108				5	0.04	0.04	4.4E-16	-3.4E-05	0.98	0.98
	SSC	PLS	601	1100-2300	9	SNV	Yes	3	4.73	5.01	0.0E+00	-2.6E-02	0.96	0.96
		iPLS	3	1152, 1336, 1890				2	4.48	4.59	-1.0E-14	8.5E-04	0.96	0.96
	Chroma (C*)	PLS	601	1100-2300	5	SNV	Yes	4	2.58	2.77	-7.1E-15	-7.3E-03	0.80	0.77
		iPLS	5	1162, 1272, 1518, 2128, 2182				5	2.40	2.48	3.0E-15	-9.2E-03	0.82	0.81

[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 period (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	1.00	1.00	0.97	0.97	0.98	0.99
								II	3-4	0.96	0.96	0.92	0.92	0.94	0.94
								III	5-8	0.97	0.97	0.99	0.99	0.98	0.98
	iPLS-DA[b]	4	1548, 1852, 2146, 2184	9	SNV	Yes	2	I	0-2	1.00	1.00	0.97	0.97	0.99	0.99
								II	3-4	0.96	0.96	0.93	0.93	0.95	0.95
								III	5-8	0.98	0.98	0.99	0.99	0.99	0.99
Microwave heating	PLS-DA	601	1100-2300	9	SNV	Yes	6	I	0-3	0.99	0.99	0.97	0.97	0.98	0.98
								II	4-5	0.95	0.92	0.87	0.87	0.91	0.89
								III	6-8	0.98	0.97	0.96	0.96	0.97	0.96
	iPLS-DA	4	1126, 1154, 1620, 2192	9	SNV	Yes	3	I	0-3	0.99	0.98	0.97	0.97	0.98	0.98
								II	4-5	0.96	0.96	0.85	0.84	0.91	0.90
								III	6-8	0.97	0.97	0.98	0.98	0.97	0.98

[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.

Figure 3a - interactive

Click here to download Supplementary Interactive Plot Data (CSV): Figure 3a - interactive.csv

Figure 3b - interactive

Click here to download Supplementary Interactive Plot Data (CSV): Figure 3b - interactive.csv