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A new application of NIR spectroscopy to describe and predict purees quality from the non-destructive apple measurements

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Highlights

Texture and taste of cooked purees could be predicted from the spectra of raw apples.

Apples and purees were well classified by NIRS according to the studied factors.

NIRS could predict acceptably quality traits of both apples and purees.

Abstract

The potential of NIRS was investigated on both apples and purees to (i) examine factors involving quality variability (variety, agricultural practice, cold storage, puree mechanical refining level) and (ii) establish the link between quality traits before and after processing in order to predict the quality characteristics of purees from spectral information of raw apples. Apples and purees were well-classified at over 82% and 88% according to varieties and storage times respectively. The PLS models showed a good ability to estimate puree characteristics from spectra acquired on corresponding apples such as viscosity ($R^2 > 0.82$), cell wall content ($R^2 > 0.81$) and also dry matter ($R^2 > 0.83$), soluble solids content ($R^2 > 0.80$) and titratable acidity ($R^2 > 0.80$). NIR technique should be a useful tool for industry insofar as it can give a reliable assessment of texture and taste of the final products based on the non-destructive fresh materials evaluation.

Key words: *Malus domestica Borkh*, Near infrared spectroscopy, PLS models, discriminant analyses, apples and purees

1. Introduction

Apple is one of the most widely cultivated fruits around the world (totally 68.6 million tons in 2018 (USDA, 2018)), consumed both as fresh fruits and processed products. The fruit could be processed into various products to meet consumers' basic nutritious demand. Among them, apple puree has recently been reported to be a good source of polysaccharides (Le Bourvellec, Bouzerzour, Ginies, Regis, Plé, & Renard, 2011) and antioxidant compounds (Loncaric, Dugalic, Mihaljevic, Jakobek, & Pilizota, 2014; Oszmiański, Wolniak, Wojdyło, & Wawer, 2008). Additionally, apple purees can be used in the food industry as the basic ingredient of many fruit-based products such as jams, preserves or compotes, yogurts and pie fillings (Defernez, Kemsley, & Wilson, 1995).

However, the modifications of the initial physical structure, color and composition, which occur during processing, often make difficult for fruit processors to know and predict the quality characteristics of purees according to the raw apples. Qualities of apple purees depend on complex interactions between process conditions and raw material characteristics. These in turn are determined by the genetic diversity (varieties), pedoclimatic conditions, agricultural practices, maturity stages, and storage periods (Espinosa-Muñoz, Symo□eaux, Re□ard, Biau, & Cuvelier, 2012; Espinosa-Muñoz, To, Symo□eaux, Re□ard, Biau, & Cuvelier, 2011; Keenan, Brunton, Butler, Wouters, & Gormley, 2011; Picouet, Landl, Abadias, Castellari, & Viñas, 2009). Apple puree manufacturers therefore encounter difficulties to maintain the expected and constant quality level of the final apple products. Until now, the research studies regarding the quality assessment of apple purees have been mainly focused on the changes in polyphenol contents and total antioxidant activity (Loncaric, Dugalic, Mihaljevic, Jakobek, & Pilizota, 2014; Sukhonthara, Kaewka, & Theerakulkait, 2016), color (Oszmiański, Wolniak, Wojdyło, & Wawer, 2008), ascorbic acid (Picouet, Landl, Abadias, Castellari, & Viñas, 2009), organic acids (Bengoechea *et al.*, 1997), sugars (Keenan, Brunton, Butler, Wouters, & Gormley, 2011), polysaccharides (Le Bourvellec, Bouzerzour, Ginies, Regis, Plé, & Renard, 2011), rheological properties (Espinosa-Muñoz, Renard, Symoneaux, Biau, & Cuvelier, 2013; Espinosa-Muñoz, Symoneaux, Renard, Biau, & Cuvelier, 2012) and sensory appreciation (Espinosa-Muñoz, To, Symoneaux, Renard, Biau, & Cuvelier, 2011). However, almost all of these quality parameters have been measured through specific laboratory analyses, such as chromatography, which are time-consuming, expensive and not suitable for fast and numerous characterizations. Consequently, the development of rapid, accurate and reliable methods is required to control the quality of the raw apples and processed purees, and meet the ever-increasing demands for consistent and high quality fruit products.

Near infrared spectroscopy (NIRS) has been increasingly used for the safety inspection and quality assessment of agricultural products (Nicolai *et al.*, 2007). It has several advantages such as rapid spectrum acquisition, limited preparation requirements and no chemical waste, but it requires an initial calibration step, which is time consuming. Indeed, on a set of samples, representative of the expected variability, both NIRS spectra and their corresponding reference data are needed to establish predictive models using multivariate statistical and mathematical data analyses. Several parameters can thus be evaluated from a single spectrum, with varying precision. Intensive investigations using NIRS have been reported regarding the measurement of apple internal attributes in the past decades (Nicolai *et al.*, 2007). Satisfactory evaluation results are reported for soluble solids contents (Peirs, Tirry, Verlinden, Darius, & Nicolaï, 2003), dry matter (McGlone, Jordan, Seelye, & Clark, 2003), titratable acidity (Liu & Ying, 2005), starch index (Menesatti *et al.*, 2009), chlorophyll content (Zude, Truppel, & Herold, 2002), firmness (Zude *et al.*, 2006), individual sugars (Liu, Ying, Yu, & Fu, 2006) and antioxidant capacity (Schmutzler & Huck, 2016). Further, NIRS spectra are shown to classify apples according to varieties (Luo *et al.*, 2011), geographical origins (Bobelyn *et al.*, 2010) and postharvest storage periods (Camps, Guillermin, Mauget, & Bertrand, 2007; Giovanelli, Sinelli, Beghi, Guidetti, & Casiraghi, 2014).

Thus, NIRS can assess a diversity of quality traits in raw apples and processed products, while some of the puree characteristics are directly linked to those of the raw fruit. We therefore can suppose that NIRS spectra of the raw fruits could be used to predict the properties of the processed products, here purees, at least given a constant process operation. However, as far as we know, there is no literature related to the feasibility of using NIRS to evaluate the changes of apple puree properties and to trace back to their corresponding raw apple quality. The challenge here was to assess the possibility of predicting the properties of processed fruit products based on the raw fruit material spectral information, and so, to provide practical and suitable strategies to estimate the quality potential of fruits, to monitor their processing, and to control the quality of fruit products.

The specific objectives of our current work were to assess the potential of NIRS to 1) detect different factors such as variety, fruit thinning, storage period and mechanical puree refining on apples and/or their corresponding purees, 2) evaluate the quality traits of interest in both apples and the corresponding purees such as textural/rheological properties, soluble solids content, titratable acidity, dry matter content, insoluble solids content 3) and then establish the links between fruit materials before and after processing.

2. Materials and methods

2.1 Fruit materials

2.1.1 Apples

The experiment was conducted on three apple varieties: ‘Golden Smoothee’, ‘Golden Delicious’, and ‘Granny Smith’ during two subsequent harvesting seasons, 2016 and 2017, that are summarized in a supplementary figure **(Suppl. Figure 1)**. In 2016, 240 ‘Golden Smoothee’ apples were harvested from the experimental orchard of INRA (Drôme, France). In 2017, 480 ‘Golden Delicious’ and 240 ‘Granny Smith’ apples were obtained from the experimental orchard at La Pugère (Bouches du Rhône, France).

Two fruit thinning levels were also compared during the ripening of ‘Golden Delicious’ apples in 2017. For this, trees were thinned 40 days after flowering (on June 2^{nd}), and the treatment named Th+ corresponded to 50 to 100 fruits/tree (a standard commercial fruit load) and Th- to 150-200 fruits/tree (highly loaded trees). The 'Golden Smoothee' in 2016 and 'Granny Smith' in 2017 grew under regular fruit thinning (Th-). After harvesting (Golden Smoothee on September 14th, 2016, 'Golden Delicious' on September 11th, 2017 and 'Granny Smith' on September 25th, 2017), apples were kept in a cold storage chamber at 4°C and at around 90% of humidity during one, three and six months (respectively T1, T3 and T6), except the first group (T0) for which apples were analyzed and processed the day after harvest. These storage durations were chosen in order to increase the fruit variability linked to firmness and biochemical changes, such as demethylation and depolymerization of pectins (Billy, Mehinagic, Royer, Renard, Arvisenet, Prost, et al., 2008). Each set (T0, T1, T3 and T6) was divided into two sub-groups. The first one was dedicated for fresh apple characterization and the second one for processing. For characterization, three replicates of 10 apples, representative of the total apple set, were analyzed after one night temperature equilibration at 23°C.

First, nondestructive measurements (NIR, color, ethylene releasing rate, fruit weight), and then texture tests (puncture mean load and puncture linear distance) were performed on each apple. After that, each apple was cored and divided as described by Bureau *et al.* (Bureau, Scibisz, Le Bourvellec, & Renard, 2012) in order to create, for each replicate of ten apples, three batches of 40 pieces representative of each apple. The pieces were immediately put in liquid nitrogen to avoid any oxidization. Finally, one batch was stored at -20 °C and then was subsequently freeze-dried to evaluate the alcohol insoluble solids (AIS) contents. The other two batches were stored at -80°C for biochemical characterization measurement.

2.1.2 Purees

For each raw apple condition, three replicates of apple puree were produced with 4 kg of apples each. After sorting and washing, apples were cored and cut in 8 portions, then processed in a multi-functional processing system (Roboqbo, Qb8-3, Bentivoglio, Italy) following a Hot Break recipe: cooked at 95°C for 5 min at a 1500 rpm grinding speed, then cooled down to 65°C while maintaining the grinding speed. Half of the batch was refined at 0.5 mm using a Robot Coupe C80 automatic refiner (Robot Coupe SNC, Vincennes, France) in order to study two levels of granularity: non-refined (NR) and 0.5 mm refined (Ra). Finally, processed purees were conditioned in hermetically sealed cans, then placed and cooled at 23 °C before measurements, which took place the next day.

2.2 Determination of quality traits

2.2.1 Color

The skin color (un-blushed and blushed sides) was determined using a CR-400 chromameter (Minolta, Osaka, Japan) and expressed in the CIE 1976 L*a*b* color space (illuminant D65, 0° view angle, illumination area diameter 8 mm). The puree color was measured three times through a dedicated glass cuvette using the same method and equipment.

2.2.2 Ethylene production

Each group of ten apples was put in a hermetic jar at 23°C for 1 hour, and ethylene production was analyzed by taking 500 µL of the headspace and injecting it in gas chromatography (Agilent, California, United States) equipped with a porapak Q column and a FID detector and expressed in nmol kg^{-1} h^{-1}.

2.2.3 Fruit texture and puree rheology

Fresh apple texture was evaluated by a puncture test using a multipurpose texture analyzer (TAPlus, Lloyd Instruments, Farenham, UK). The puncture tests were operated with a punch probe (diameter 1.2 mm), which could penetrate up to a depth of 17 mm into each peeled section of apple. Firmness was then evaluated as the mean load value calculated by the division of penetration energy by the height of testing. Crunchiness of apple flesh (Gregson & Lee, 2002) was estimated as the linear distance values from the area under the force-distance curve in the range of 10 mm at the load plateau, consisting in summing the lengths between consecutive points.

The puree rheological measurements were carried out using a Physica MCR-301 controlled stress rheometer (Anton Paar, Graz, Austria) at 22.5 °C. The flow curves were performed after a pre-shearing period of 1 minute at 50 s^{-1} followed by 5 minutes at rest. The viscosity was measured at a rate of 1 point every 15 seconds, at a co□trolled shear rate ra□ge of [10; 250] s^{-1} on a logarithmic ramp. The value of the viscosity at 100 s^{-1} η_{100} was kept as an indicator of the puree viscosity. As often used to model fruit purees (Colin-Henrion, Cuvelier, & Renard, 2007), the complete flow curves were fitted with a power-law viscosity model as described by Eq. 1.

$$\eta = K\ \dot{\gamma}^{n-1} \qquad (Eq1)$$

where η is the apparent viscosity (Pa.s), $\dot{\gamma}$ the shear rate (s^{-1}), K the consistency parameter, and *n-1* the flow parameter.

2.2.4 Biochemical characterization of apples and purees

Soluble solids content (SSC) was determined with a digital refractometer (PR-101 ATAGO, Norfolk, VA, USA) and expressed in °Brix at 20°C. Titratable acidity (TA) was determined by titration up to pH 8.1 with 0.1 mol/L NaOH and expressed in mmol H^+/kg of fresh weight (FW) using an autotitrator (Methrom, Herisau, Switzerland). Contents of sugars (glucose, fructose, and sucrose) and malic acid were quantified using an enzymatic method with kits for food analysis (Sigma-Aldrich, Deisenhofen, Germany) and expressed in g kg^{-1} FW. These measurements were performed with a SAFAS flx-Xenius XM spectrofluorimeter (SAFAS, Monaco). The dry matter content (DMC) was estimated with the difference between the weight values of fresh samples and of freeze-dried samples upon reaching constant weight (freeze-drier, 5 days). Content of alcohol insoluble solid (AIS) was evaluated using the method proposed by Renard (Renard, 2005) and expressed as the ratio on both fresh weight (FW) and dry matter weight (DW). Three biological replicates were obtained for each biochemical trait and each sample.

2.3 FT-NIR spectrum acquisition

The spectral data of apples and purees were both acquired with a multi-purpose analyzer spectrometer (Bruker Optics®, Wissembourg, France), which provides diffuse reflectance measurements with a spectral resolution of 2 nm from 800 to 2500 nm. For each spectrum, 32 scans were recorded and averaged. The spectral acquisition and instrument adjustments were controlled by OPUS software Version 5.0 (Bruker Optics®). The apples were placed on an automated 30-positions sample wheel, each position corresponding to a measured area of 18 mm diameter. For each intact apple, two spectra were collected (on the blushed and un-blushed sides) though the 18 mm diameter areas at 23°C. Puree were transferred into 10 mL glass vials (5 cm height x 18 mm diameter) which were placed on the automated sample wheel of the spectrophotometer. Each puree sample was measured three times on different aliquots. A reference background measurement was automatically activated before each data set acquisition using an internal Spectralon reference.

2.4 Statistical analyses and chemometrics

After ensuring the normal distribution of dataset, the results were presented as mean values and the data dispersion within our experimental dataset expressed as standard deviation values (SD). Analysis of variance (ANOVA) was carried out to determine the significant differences due to the tested factors on both apples and purees using XLSTAT (version 2018.5.52037, Addionsoft SARL, Paris, France) data analysis toolbox. The pairwise comparison between means was performed using Tukey's test at the 95% level of certainty ($p < 0.05$(*), 0.01 (**) and 0.001 (***)). For apples, a one-way ANOVA was applied to access the effect of storage period on 'Golden Smoothee' in 2016 and 'Granny Smith' i□2017; a two-way ANOVA concerned the effects of storage period and fruit thinning on 'Golden Delicious' in 2017. For purees, a two-way ANOVA accessed the effects of storage periods and refining treatments on 'Golden Smoothee' and Granny Smith, and a three- way ANOVA for 'Golden Delicious' in terms of fruit thinning, storage periods and puree refining levels. Pearson's determination coefficients (R^2) were calculated in order to study the significance of the relationship between apples and purees and then output as an heat map using R software (version 3.5.2) (R Core Team, 2018) and the additional package named 'ComplexHeatmap' (Gu, Eils, & Schlesner, 2016).

Spectral pre-processing and multivariate data analysis were performed with Matlab 7.5 (Mathworks Inc. Natick, MA) software using the SAISIR package (Bertrand & Cordella, 2008). All the NIR data were pre-processed with standard normal variate (SNV) and a derivative transform calculation (Savitzky–Golay method, gap size = 11, 21, 31, 41) of first or second order. Each of the preprocessing methods was tested in the discrimination models. As SNV pre-processing had the best performances to correct multiplicative interferences and variations in baseline shift, the results shown are those obtained with the SNV pretreatment. Principal Component Analysis (PCA) and Factor Discriminant Analysis (FDA) were carried out on spectral data to evaluate the possibility to discriminate samples according to the tested factors (cultivars, thinning and storage). The specificity and sensitivity values of FDA discriminations, which help for a better evaluation of the rate of sample differentiation, were calculated by the already reported method of Nargis (Nargis *et al.*, 2019). The Partial least-square (PLS) regression method was used to develop predictive models of the quality traits of interest in apples and purees. The whole spectral dataset included 840 spectra of apples and 240 spectra of purees. The dataset was randomly split, two third of dataset (560 spectra of apples and 160 spectra of purees) were used for calibration and one third of dataset (280 spectra of apples and 80 spectra of purees) for validation. The procedure was repeated 10 times in order to obtain the suitable dimensions of the

PLS models. The latter performance was described by the root mean square error of calibration (RMSEC), the root mean square error of validation (RMSEV), the number of latent variables (LVs), the determination coefficient (R^2) between the predicted and measured parameters and the RPD (Residual Predictive Deviation) value as described by Nicolai (Nicolai *et al.*, 2007).

3. Results and discussion

3.1 Apple and puree characteristics measured by classical methods

3.1.1 Fresh apples

In this experiment, three cultivars, two agricultural conditions and a cold storage for 6 months provided an interesting apple fruit variability (**Figure 1a and 1b**). Clear discriminations were shown between the different storage periods along the first principal component, and apple varieties and thinning levels along the second principal component (**Figure 1a**). 'Granny Smith' was clearly differentiated from the two 'Golden' cultivars. Remarkably, the two non-thinned 'Golden' samples were close to each other (blue in 2016 and red in 2017), in spite of different growing seasons and locations, while the thinned samples were clearly differentiated. The most discriminant quality traits were: mean load, linear distance, AIS content (FW and DW), TA, malic acid content, ethylene production rate and color changes (L*, a* and b*) on the first principal component, and SSC, DMC and sucrose content on the second principal component (**Figure 1b**). The totality of the acquired data is presented in a supplementary table (**Suppl. Table 1**).

During cold storage, mean load, linear distance and AIS content (FW and DW) decreased remarkably ($p < 0.001$) in all apples, indicating an intensive reduction of apple firmness, crunchiness and cell wall material contents (Johnston, Hewett, & Hertog, 2002). Good correlations were observed between AIS and mean load (R^2 =0.78 in 'Golden Smoothee', R^2=0.75 in 'Granny Smith', R^2 =0.82 in 'Golden Delicious'). The acidity in all apples decreased significantly with storage ($p < 0.001$) at a large range from 103.4 to 26.5 meq/kg FW for TA and 6.5 to 2.3 g/kg FW for malic acid. The ethylene production rate increased and then decreased during storage with significant changes ($p < 0.001$). All color parameters (L*, a* and b*) increased clearly for all apples, linked to a degreening and a yellowing during the long-term storage. The changes of all individual sugar contents were significant in 'Golden Smoothee' ($p < 0.05$) and 'Golden Delicious' ($p < 0.001$), but not in 'Granny Smith' ($p > 0.05$). For 'Golden Delicious', SSC and DMC from thinned trees (Th +) appeared to be significantly ($p < 0.001$) higher than from non-thinned trees (Th-).

3.1.2 Apple purees

The fresh apple variability described above affected the characteristics of the corresponding non-refined (NR) purees cooked using the same recipe (**Figure 1c and 1d**). The NR purees were discriminated according to the apple variety, fruit thinning and storage periods (**Figure 1c**). The first principal component was positively correlated to TA, content of malic acid, AIS (DW and FW) and rheological parameters (η_{100}, K), and negatively linked with colors (L*, b*) and fructose content. The storage periods could be well-classified with this component. The second principal component was highly related to DMC, sucrose content, SSC and AIS content (FW) allowing the separation of varieties and fruit thinning conditions.

In all NR purees, clear decreases ($p < 0.001$) of TA, malic acid and AIS (in DW) were observed during storage, which were highly consistent with their changes in raw apples. At the same time, the rheological properties (η_{100} and K) decreased, with statistically significant differences ($p < 0.01$) in all NR purees, but not in Ra purees (**Suppl. Table 2**). A good correlation was found between AIS expressed in fresh weight (FW) and the values of η_{100} in 'Golden Smoothee' (R^2=0.77), 'Granny Smith' (R^2=0.73) and non-fruit thinned (Th-) 'Golden Delicious' (R^2=0.84), meaning there was a good relationship between cell wall content and viscosity in NR purees. Visually perceptible differences of color with an increase of L* and b* (with $\Delta E > 2$) were detectable only after 6 months of storage for 'Golden Delicious' and 'Golden Smoothee' (Hunter, & Harold, 1987). Fructose content, as the major individual sugar, increased significantly ($p < 0.001$) in 'Golden Smoothee' and 'Golden Delicious' purees during storage, but not for 'Granny Smith', again in good agreement with the behavior observed in the raw fruits.

The changes of SSC, sucrose content and DMC in purees were still the major discriminative contributors for apple varieties and fruit thinning conditions during puree processing. Obvious differentiations were observed for SSC and sucrose content between 'Granny Smith' purees and the other purees, in accordance with their changes in raw apples. In 'Golden Delicious', tree thinning (Th+) led to a significant increase ($p < 0.001$) of DMC both in apples and their corresponding processed purees at each storage period (supplementary information, **Suppl. Table 1 and 2**), in accordance with the fact that the thinned apples, in addition to being larger, also accumulates more cell materials per volume unit (Palmer, Harker, Tustin, & Johnston, 2010). Additionally, the apples of the tree thinning (Th+) gave purees more viscous with significant higher values of η_{100} and K ($p < 0.001$) than the non-thinning condition (Th-). The tree thinning treatments, by affecting individual apple growth potential, affected physical properties of raw apples and processed purees, including their viscosity. Small fruits from non-thinned trees (Th-) resulted in less viscous purees than large fruits from thinned trees.

Concerning the refined (Ra) purees, an expected clear reduction was obtained for both AIS content (in DW) and viscosity (η_{100}) after refining (**Suppl. Table 2**). That could be due to the loss of insoluble fibers in the removed particle fraction (Colin-Henrion, Mehinagic, Renard, Richomme, & Jourjon, 2009) leading to a loss of puree viscosity (Espinosa-Muñoz, To, Symoneaux, Renard, Biau, & Cuvelier, 2011; Leverrier, Almeida, & Cuvelier, 2016).

3.1.3 Relationship between the fresh apples and puree characteristics

In order to study the link between physical and chemical parameters of raw apples and their processed purees, the coefficients of determination (R^2) were calculated with the dataset including all three varieties under two thinning conditions (Th+ and Th-) and two refining levels and are displayed as heat maps for R^2 values from red ($R^2 > 0.8$) to blue ($R^2 < 0.2$) (**Figure 2**). A clear similarity was observed between the two maps (**Figure 2a and 2b**) with the same blue and red areas. Between all apples and their processed purees, high R^2 values (0.92 in NR and 0.91 in Ra) were obtained for TA.

Acceptable correlations were also found for SSC (0.79 in NR and 0.81 in Ra), DMC (0.72 in NR and 0.73 in Ra) and malic acid content (0.65 in NR and 0.61 in Ra). For the AIS (DW) contents, good correlations (R^2) were obtained for each variety between raw apples and NR purees (not for Ra purees): 0.76 in 'Golden Smoothee', 0.83 in 'Granny Smith' and 0.77 in 'Golden Delicious', but lower when using all NR purees (R^2= 0.65). Moreover, acceptable correlations (R^2> 0.71) were obtained between texture characteristics (mean load and linear distances) of all apples and rheological parameters (η_{100} and K) of their corresponding purees, whether non-refined (NR) (**Figure 2a**) or refined (Ra) (**Figure 2b**). The rheological variations in processed purees under the effects of different genotypes, storage periods and refining treatments were consistent with the textural changes in apples. However, no significant correlations (R^2 < 0.44) were found for individual sugars (glucose, sucrose and fructose) between all apples and their purees (NR and Ra), probably because: i) these concentrations changed less during long-term storage than TA and malic acid content, and ii) water content varied during thermal processing and refining treatments.

The good correlations of acidity (TA and malic acid content), SSC, DMC and physical properties (textual and rheological parameters) between apples and their purees were in line with PCA results (**Figure 1b and 1d**). The chemical and physical variations in purees were shown to be potentially linked to the raw apple properties.

3.2 Apple and puree characteristics measured by NIRS

ANOVA was performed on the SNV pre-treated NIR spectra of apples and processed purees (**Figure 3**), in order to point out the wavelengths that varied during processing. According to the F-values, the variability was clearly higher for the spectra of apples (**Figure 3a and 3b**) than those of purees (**Figure 3c and 3d**), as could be expected given that each puree was prepared from 4 kg of fruit. For raw apples, the effect of variety (F-values of 800) was higher than the effect of storage (F-value of 120) (**Figures 3a and 3b**). However, after processing into purees, the opposite conclusion was obtained: the effect of storage (F-values of 110) was almost three times higher than the effect of variety (F-value of 40) (**Figure 3c and 3d**). Combine with their averaged spectral results (not shown), when apples were processed into puree, the peaks at 1930 nm in apples (**Figure 3a**) were not variable in purees (**Figure 3c**), demonstrating that the water contents had very limited variations in the purees.

3.2.1 Discrimination of fresh apples

The wavelength range with the most variability (between 1700 and 2350 nm), identified by the ANOVA (**Figure 3a**), was chosen to discriminate the effects of cultivar and storage. This range was used to perform PCA and FDA (**Figure 4a and 4b**).

The first PCA displayed the discrimination of apples according to the variety (**Figure 4a**). The first PC-score (PC1) discriminated 'Granny Smith' (GS) on the left and 'Golden Delicious' (GD) and 'Golden Smoothee' (GO) on the right, and accounted for 83.5% of the total variability. As observed for the reference data, 'Golden Smoothee' spectra were overlapped with those of 'Golden delicious'. The wavelengths at around

1880 nm, 1930 nm and 2100-2300 nm were the main contributors of the PC1 (not shown).The two bands at 1880 nm and 1930 nm are explained by the O-H combinations, which have been reported to characterize the water content in apples (Camps, Guillermin, Mauget, & Bertrand, 2007). The broad band at 2100-2300 nm corresponds to the first combination band of C-H bond of sugars or organic acids, already used to determine the concentration of individual sugars in apple juices (León, Kelly, & Dow□ey, 2005; Liu, Yi□g, Yu, & Fu, 2006). These fingerprint wavelengths are consistent with the discrimination of apple cultivars harvested in France (Camps, Guillermin, Mauget, & Bertrand, 2007).

In a second step, the different storage periods of all apples could be separated (100% of discrimination sensitivity and specificity between T0 and T1 apples, and 98.5% for sensitivity and 99.5% for specificity between T1 and T3 apples) by FDA (**Figure 4b**). It was observed that T3 and T6 apples were overlapped (**Figure 4b**), in line with their changes of mean load and linear distance (PCA could not well-classified storage periods). However, this result was inconsistent with previous report regarding well classification of storage periods of 'Golden Delicious' at 2°C by FDA (Giovanelli, Sinelli, Beghi, Guidetti, & Casiraghi, 2014). In our experiment, the strong variability and heterogeneity from different apple cultivars and fruit-thinning treatments could provide more variations of water contents and carbohydrates, and thus introduced difficulties to well classify the storage stages after 3 months (T3). The use of different storage temperatures might also be involved, with a faster evolution at 4°C than at 2°C. The relevant wavelengths were mainly located in the ranges from 1700-1900 nm and 2250 nm (not shown).

The wavelengths around 1880 nm, 1930 nm, and 2100-2300 nm could be applied to the discrimination of apple varieties, while those at 1700-1900 nm and 2250 nm could be used for the classification of apple storage periods.

3.2.2 Discrimination of apple purees

For purees, the ANOVA indicated major variations in the following wavelength ranges: 800-1050 nm, 1550-1730 nm, 1870 nm and 2100-2200 nm (**Figures 4c and 4d**). Thus, the whole wavelength range from 800 to 2500 nm was used for FDA on the spectral dataset of all purees (not well-classified with PCA). The first two factors of the FDA allowed the discrimination of the three cultivars, 'Golden Smoothee' (GO), 'Granny Smith' (GS) and 'Golden Delicious' (GD), with the discrimination specificity and sensitivity values of 86.8% and 84.6% in GD and GO apples; 84.0% and 82.2% in GD and GS apples; 88.5% and 91.9% in GD and GS apples (**Figure 4c**). The F1 and F2 coefficients were both highly correlated with the area between 800 and 1000 nm (not shown), which is known as the absorption of apple carbohydrates and water (Giovanelli, Sinelli, Beghi, Guidetti, & Casiraghi, 2014; Zude, Herold, Roger, Bellon-Maurel, & Landahl, 2006), and already used for apple cultivar classification (Bobelyn *et al.*, 2010). Purees could be classified according to the storage periods with a distinct group for T0 and T1 (91.7% of sensitivity and 95.0% of specificity), but a mixed group for T3 and T6 (**Figure 4d**). Besides the aforementioned absorbance region between 800 and 1000 nm, the wavelengths around 1400 nm and between 2100 and 2300 nm were also major contributors for discrimination of storage durations. These regions have been shown to be related to water loss and SSC variations, and could be regarded as the fingerprint wavelengths of apple storage periods (Camps, Guillermin, Mauget, & Bertrand, 2007; Giovanelli, Sinelli, Beghi, Guidetti, & Casiraghi, 2014; León, Kelly, & Downey, 2005).

Other interesting results were obtained with the FDA applied on ‘Granny Smith’ purees taking into account the refining levels and the storage durations (not shown). According to the F1 and F2 axes, the two refining levels (Na and Ra) were separated both at T0 and T1, but not at T3 and T6. This result is highly consistent with the rheological changes of refined and non-refined purees of ‘Granny Smith’ (**Suppl. Table 2**). This refining treatment led to stronger losses of viscosity and cell wall (AIS) content before the first month of apple storage (T1), compared to purees prepared after three months (T3 and T6).

3.3 Prediction of quality traits by NIRS

In this study, we tested the ability of NIR spectra and reference data coupled with PLS to predict the physical and biochemical parameters of: (1) all apples from their NIR spectra (**Suppl. Table 3**); (2) all processed purees (NR and Ra) from their NIR spectra (**Suppl. Table 4**); (3) and all purees from the spectral information of apples (**Tables 1 and 2**).

3.3.1 Prediction of quality traits by NIRS on fresh apples

The prediction models were developed based on the 840 NIR spectra of apples combining 3 varieties, 2 years, 2 fruit thinning practices and 4 storage periods (**Suppl. Table 3**). Selected results ($R^2 > 0.8$ obtained for the validation and RPD values > 2) were further discussed.

The prediction results of AIS content (R^2=0.85 expressed in dry weight and R^2=0.83 in fresh weight) during cold storage stood out in **Suppl. Table 3**. The prediction of AIS content has already been studied but using the destructive mid-infrared technique on freeze-dried apple powder (Canteri, Renard, Le Bourvellec, & Bureau, 2019), and using NIRS to predict AIS content on ‘Golden Delicious’ apples during seven months storage at 2 ± 0.5°C with a R^2 of 0.96 (Lovász, Merész, & Salgó, 1994). The lower R^2 value in our study was probably in relation with the fact that three varieties and fruit thinning conditions were introduced in the same models. For the crunchiness (linear distance), the prediction result was acceptable (R^2=0.82, RPD=2.34), in accordance with previous results obtained on ‘Golden Delicious’, ‘Braeburn’ and ‘Fuji’ apples during a 7 months cold storage (R^2=0.84), but using the crunchiness data from sensory evaluation and the averaged NIR spectra of each group (Mehinagic *et al.*, 2003). Good predictions were obtained with DMC (R^2=0.87, RPD= 2.53) and SSC (R^2=0.81, RPD= 2.21), which were in accordance with previous studies (Giovanelli, Sinelli, Beghi, Guidetti, & Casiraghi, 2014; McGlone, Jordan, Seelye, & Clark, 2003). Moreover, acceptable correlation coefficients were obtained for TA (R^2=0.80, RPD= 2.09) and for the main organic malic acid (R^2=0.78, RPD=2.03). For the other individual sugar compounds, results were acceptable for fructose content (R^2=0.81, RPD=1.93) and sucrose content (R^2=0.81, RPD=2.14).

Consequently, in apples, NIR spectroscopy was a powerful tool to qualify the crunchiness (linear distance), SSC, TA, DMC, content of individual sugars (fructose and sucrose) and AIS. The benefit of AIS content prediction by NIRS was evident because the classical method of extraction and analysis needs a long time and lots of chemical solvents. Our models were also robust, given the large fruit variability used, with factors such as varieties, thinning practices and cold storage periods.

3.3.2 Prediction of quality traits of all purees

For purees, good predictions were observed for global parameters such as DMC (R^2=0.85, RPD=2.42) and SSC (R^2=0.92, RPD=3.12) (**Suppl. Table 4**). The higher R^2 regarding SSC in purees than in apples, could possibly due a better homogeneity of the puree samples after processing. Additionally, acceptable results were also be observed for TA (R^2=0.80, RPD=2.22). For individual compounds, results were acceptable only for fructose (R^2=0.83, RPD=2.51). For the physical properties, rheological parameters (η 100, *K* and n) and color (L*, a* and b*), only poor results were obtained in all purees (R^2 < 0.51). However, in 'Granny Smith' purees (not shown), good correlations were obtained between NIRS and η100 (R^2=0.94, RPD=6.53), and *K* (R^2=0.93, RPD=3.52), and n (R^2=0.87, RPD=2.94). It seemed NIRS provided the possibility to access the evolution of rheological parameters in 'Granny Smith' purees from different apple storage times, but this relationship was not robust if a large variability of genotypes and agricultural practices were involved. Moreover, the results were surprising for AIS which was well-predicted in the corresponding intact apples (**Suppl. Table 3**), but not in all processed purees (R^2 < 0.69, RPD < 1.59). The acceptable prediction of AIS content in apples probably depended on the good correlation between AIS and textural changes (firmness and crunchiness).

3.3.3 Prediction of puree quality traits from NIR spectra of fresh apples

In this part, PLS models were developed by combining spectral data acquired on fresh apples and reference data acquired on purees with two approaches: a) use the 48 averaged apple spectra (means of spectra of 2 faces x 10 apples by set) and the 48 reference data of their corresponding NR or Ra purees (3 replicates x 4 storage periods x 4 puree groups); b) use the 480 averaged spectra of individual apples (means of faces a and b only) and their 48 reference data of corresponding NR or Ra purees. In this case, the same values of puree characteristics were linked to the 10 apples of the same set. These two methods (a and b) obtained similar prediction results and only results of the method b taking into account the apple spectra variability are shown, for both the NR purees (**Table 1**) and Ra purees (**Table 2**).

In NR and Ra purees, good predictions were obtained for rheological parameters (η_{100}, K and n). Especially for η_{100}, impressive R^2 and RPD values were observed for NR purees (R^2=0.88, RPD=2.31) and Ra purees (R^2=0.82, RPD=2.44). Good results were also obtained for AIS content (expressed in FW and DW) in NR purees (R^2=0.81, RPD=2.23) and Ra purees (R^2=0.84, RPD=2.48). As the AIS content is one of the main contributors of puree viscosity (Leverrier, Almeida, & Cuvelier, 2016), these concomitant results between AIS content and rheological parameters could probably be related to their good correlations in purees. In all studied purees, good correlations were obtained between their AIS and viscosity behaviors (η_{100}) (R^2 =0.75), but not for the AIS and SSC values (R^2=0.32). For coloration, acceptable prediction results of b* value were obtained both in NR purees (R^2=0.81, RPD=2.19) and Ra purees (R^2=0.79, RPD=2.12). Moreover, considering the DMC, SSC and TA, the PLS regression models had a good ability to estimate each characteristic for all purees on the basis of acceptable R^2 and RPD values ($R^2 > 0.80$, RPD > 2.11). However, the NIR technique cannot be used to estimate satisfactorily the content of individual sugars (fructose, sucrose, glucose) and of malic acid of purees depending on the spectral information of raw apples.

What stands out in these results was the better predictions of some quality traits of puree from fresh apple spectra (**Table 1 and 2**) than from the puree spectra directly (**Suppl. Table 4**). It was the case for rheological parameters, R^2=0.82 from apples and $R^2 < 0.44$ from purees, possibly owing to the acceptable links ($R^2 > 0.71$) between apple texture (mean load and linear distance) and puree rheological properties (**Figure 2**). In addition, better PLS results to predict AIS content from fresh apple spectra (R^2=0.81 in FW and 0.84 in DW) were obtained than from purees spectra ($R^2 < 0.69$) (**Suppl. Table 4**), probably due to good relationships between puree viscosity and AIS content mentioned above. Besides, the prediction of DMC, SSC and TA were still acceptable in all cases. Therefore, NIR technique showed a potential to directly predict the viscosity properties, b*, AIS content, SSC, DMC and TA of processed purees using their corresponding apple spectral information directly.

Compared with the PLS models used to predict the characteristics of purees based on their own spectra **(Suppl. Tables 3 and 4)**, more LVs and lower prediction accuracy (RPD values) have generally found when models were built using the spectra of the intact apples to predict the characteristics of the processed purees. This fact has been also observed when other raw materials, e.g. meat (Meullenet, Jonville, Grezes, & Owens, 2004) or whole grain (Windham et al., 1997) were used to predict quality traits of the final cooked food. Such indirect prediction is a challenge as the spectra were not acquired on the material for which prediction was done, and because the chemical and textural traits from the material on which the spectra were acquired (the raw apples) are modified by processing. However, such predictions, albeit only semi-quantitative, are relevant for industrial use. Indeed, these developed models provide a promising solution to evaluate puree viscosity, a primary quality trait of this product, and cell wall contents (AIS), only based on spectra of fresh apples. A remarkable fact was that these predictions could not be done using the NIR spectra of the purees themselves (**Suppl. Table 4**).

4. Conclusion

As far as we know, this was the first report concerning the assessment of quality variation of apple purees depending on NIR spectral information of the corresponding raw apples. Up to now, in apple industry, manufacturers use their experience and knowhow to make blend of apples in order to obtain always the same puree. From our results, NIR had the potential to predict internal quality of apples but also that of their processed products: a reliable assessment of texture and taste of the purees could be obtained based only on spectral data of fresh apples. This opens the possibility to sort or select apples according to the expected purees. By systematically scanning all apples, this could provide some objective data to predict the final product characteristics and thus reduce waste of materials along the processing chain. Further work will be needed to investigate the interaction of the processing conditions (temperature, time, oxygen and so on) with raw apples under various growing and storage conditions, so as to provide guidance for adapted processing procedures to reach stable final puree qualities.

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Figure captions

Figure 1. Principal Component Analysis of physical, physiological and biochemical compositions for: apples **(a)** and processed NR (no refined) purees **(c)** in three varieties (GO: 'Golden Smoothee' , GD: 'Golden Delicious' and GS: Granny Smith) growing under two different thinning conditions (Th+ marked with red solid circle and Th- with red dotted circle) and stored at 4°C from harvest (T0), 1 (T1), 3 (T3) and 6 (T6) months. Correlation plot of the first principal components for apples **(b)** and NR purees **(d)**.

Figure 2. Determination coefficient (R^2) of all physical and biochemical parameters between the 'Golden Smoothee', 'Granny Smith' and 'Golden Delicious' apples (titled with "F") and their processed purees (titled with "P"): **(a)** raw apples and non-refined (NR) purees; **(b)** raw apples and refined (Ra) purees.

Figure 3. ANOVA results of the SNV pre-treated NIR spectra between 800 and 2500 nm: **(a)** effect of variety on all apples spectra; **(b)** effect of storage period on all apples spectra; **(c)** effect of variety on all purees spectra; **(d)** effect of storage period on all purees spectra;

Figure 4. Factorial maps of the SNV pre-treated NIR spectra of all apples between 1700 and 2350 nm or all purees between 800 and 2500 nm: **(a)** Principal Component Analysis showing apples cultivars; **(b)** the Factorial Discriminant Analysis of storage periods of apples; **(c)** Factorial Discriminant Analysis of cultivars of all purees; **(d)** Factorial Discriminant Analysis of storage periods of all purees.

'Golden Smoothee' (GO), 'Golden Delicious' (GD), 'Granny Smith' (GS); storage duration at 4°C from harvest (T0), 1 (T1), 3 (T3) and 6 (T6) months.

Figures

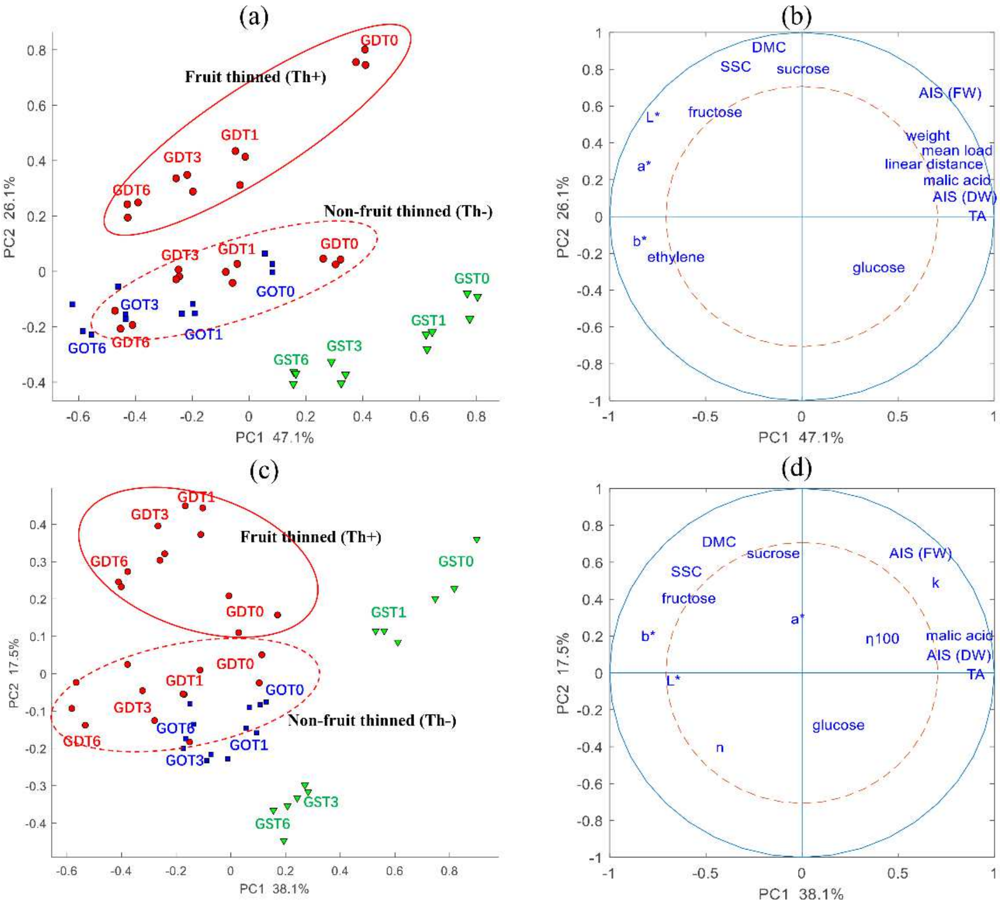
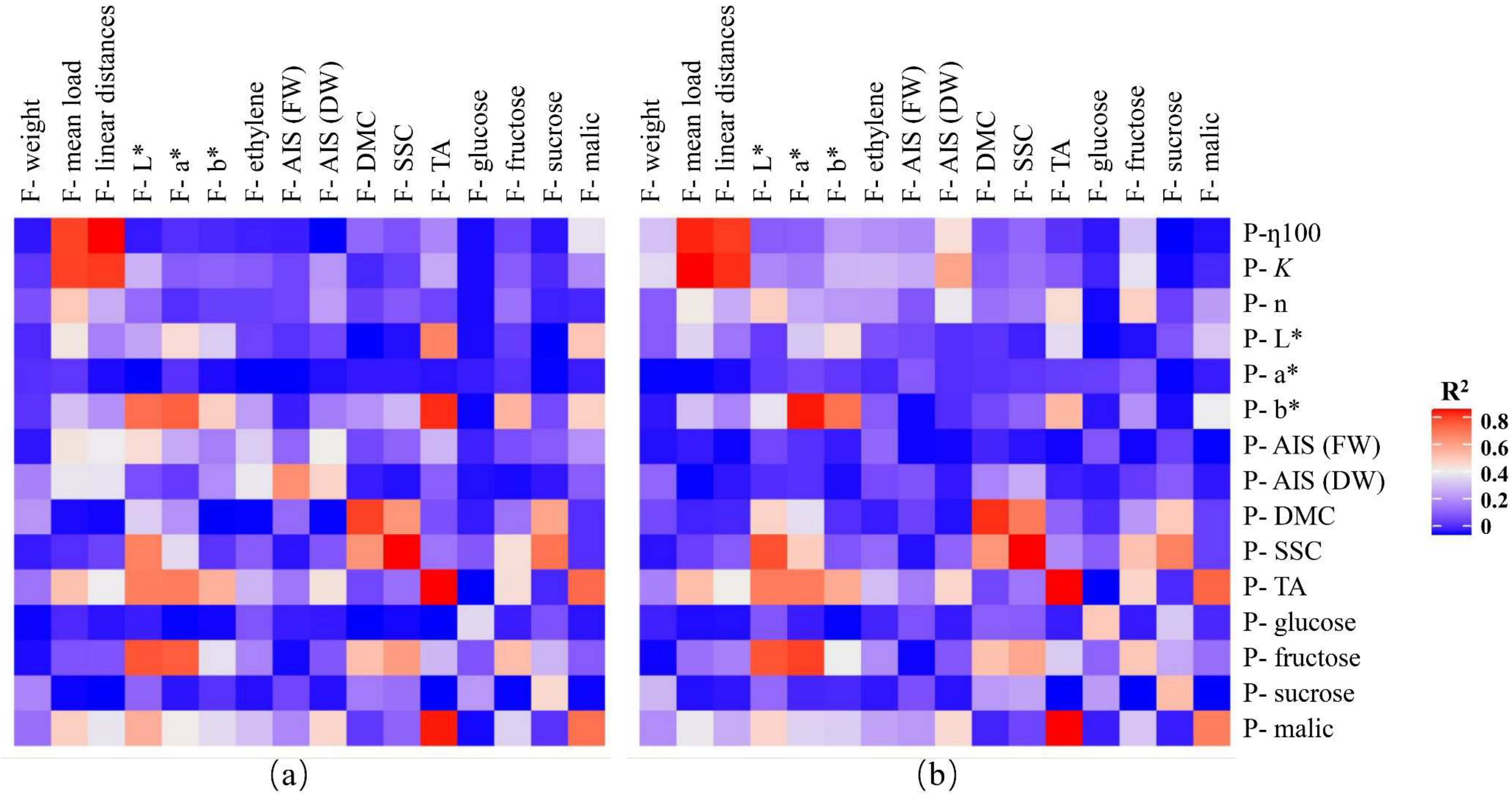


Figure 1



F- weight
F- mean load
F- linear distances
F- L*
F- a*
F- b*
F- ethylene
F- AIS (FW)
F- AIS (DW)
F- DMC
F- SSC
F- TA
F- glucose
F- fructose
F- sucrose
F- malic
P-η100
P- K
P- n
P- L*
P- a*
P- b*
P- AIS (FW)
P- AIS (DW)
P- DMC
P- SSC
P- TA
P- glucose
P- fructose
P- sucrose
P- malic
R²
0.8
0.6
0.4
0.2
0
(a)
(b)

Figure 2

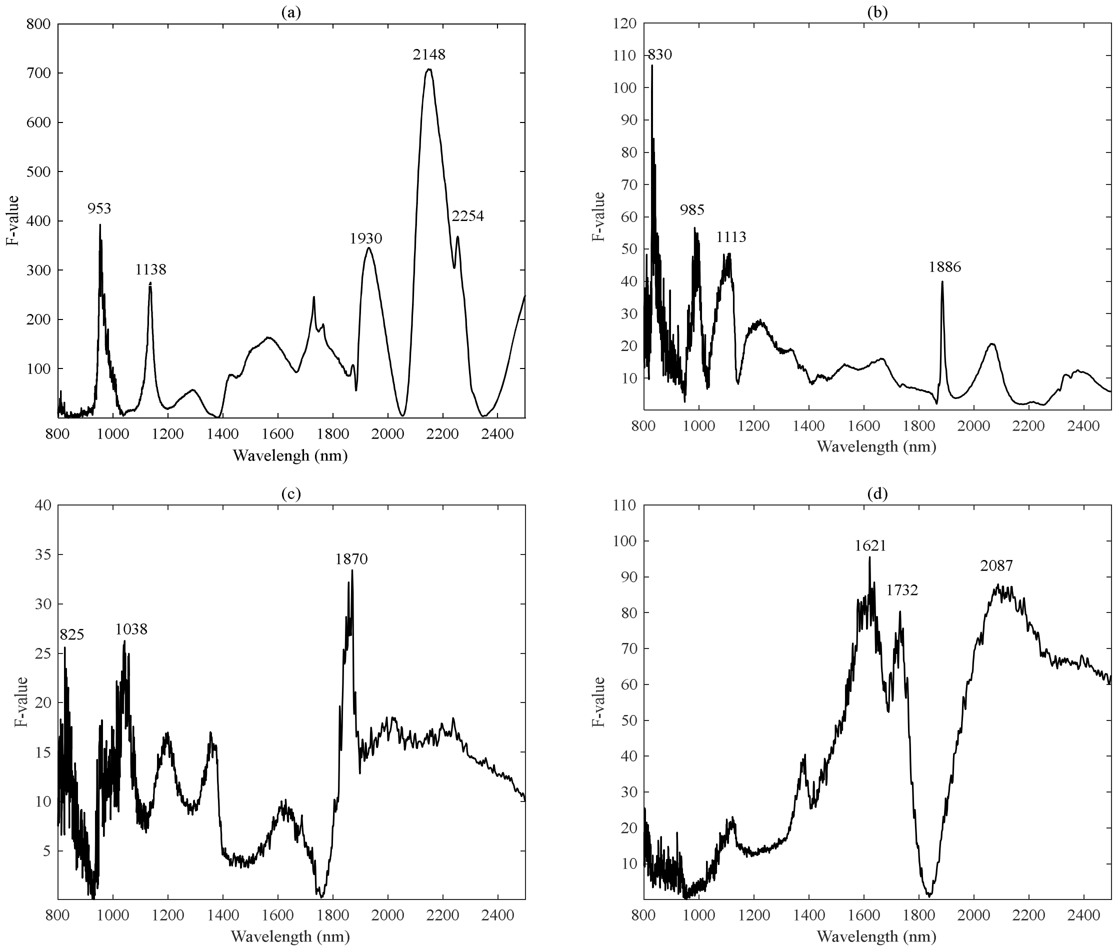

(a)
F-value
Wavelengh (nm)
953
1138
1930
2148
2254
(b)
F-value
Wavelength (nm)
830
985
1113
1886
(c)
F-value
Wavelength (nm)
825
1038
1870
(d)
F-value
Wavelength (nm)
1621
1732
2087

Figure 3

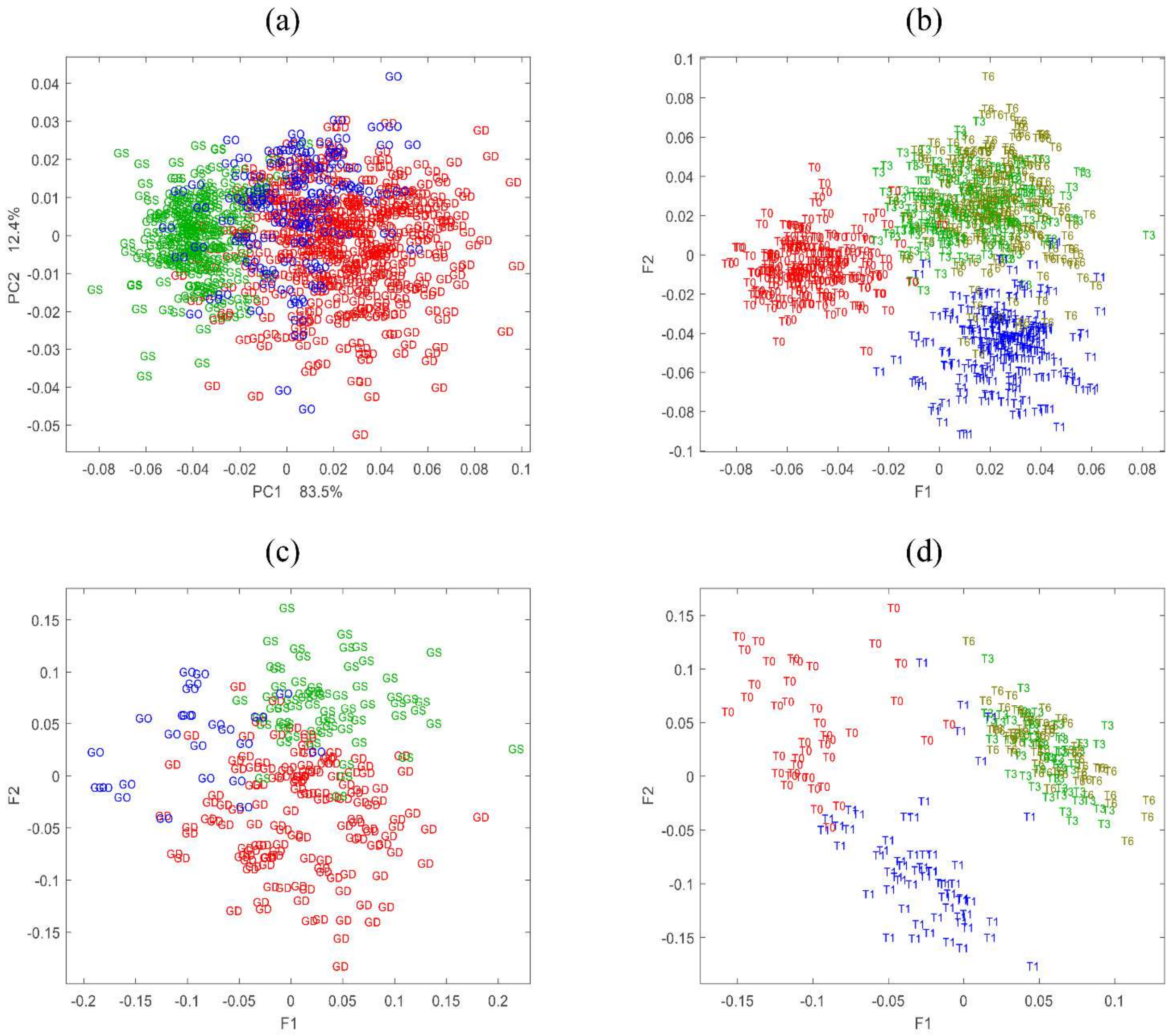


Figure 4

Table 1. Prediction of puree quality traits from spectral data of fresh apples: PLS (Partial Least Squares) results using NIR spectra of fresh apples from three varieties ('Granny Smith', 'Golden Delicious' and 'Golden Smoothee'), two thinning conditions and two harvest seasons, at 4 cold storage durations (0, 1, 3 and 6 months) for prediction of quality traits of non-refined (NR) purees.

			Calibration n=320		Validation n=160				
Parameter	range	SD	r^2	RMSEC	R^2	RMSEV	LVs	RPD	spectral range(nm)
CSR (η_{100})	0.49-1.45	0.19	0.89	0.06	0.88	0.08	10	2.31	900- 2500
viscosity-*K*	16.8-59.5	11.24	0.79	5.0	0.79	5.2	12	2.15	900- 2500
viscosity-n value	0.06-0.39	0.07	0.83	0.03	0.82	0.03	12	2.06	900- 2500
L*	44.0-53.5	1.9	0.81	0.8	0.81	1.1	10	1.77	900- 2500
a*	-(5.0-3.4)	0.3	0.48	0.3	0.46	0.3	10	1.36	900- 2500
b*	9.2-23.0	3.5	0.84	1.4	0.81	1.6	12	2.19	900- 2500
AIS（mg/g DW）	114.0-171.7	32.6	0.82	16.4	0.80	16.3	11	2.00	900- 2500
AIS（mg/g FW）	19.3-48.9	5.8	0.82	2.5	0.81	2.6	13	2.23	900- 2500
DMC (g/g FW)	0.16-0.23	0.02	0.84	0.01	0.83	0.01	12	2.11	900- 2500
SSC (°Brix)	10.5-18.6	2.2	0.85	0.9	0.80	1.0	11	2.25	900- 2500
TA (meq/kg FW)	25.0-103.9	20.0	0.83	8.3	0.80	9.4	11	2.14	900- 2500
glucose (g/kg FW)	13.5-25.4	3.1	0.65	1.8	0.60	2.0	10	1.55	900- 2500
fructose (g/kg FW)	40.0-98.7	17.2	0.80	7.6	0.73	9.1	11	1.90	900- 2500
sucrose (g/kg FW)	32.2-118.5	22.0	0.80	9.6	0.76	11.1	11	1.98	900- 2500
malic (g/kg FW)	2.4-9.0	1.5	0.77	0.7	0.76	0.8	10	1.91	900- 2500

Table 2. Prediction of puree quality traits from spectral data of fresh apples: PLS (Partial Least Squares) results using NIR spectra of fresh apples from three varieties (‘Granny Smith’, ‘Golden Delicious’ and ‘Golden Smoothee’), two thinning conditions and two harvest seasons, at 4 cold storage durations (0, 1, 3 and 6 months) for prediction of quality traits of refined (Ra) purees.

T			Calibration n=320		Validation n=160				
Parameter	range	SD	r^2	RMSEC	R^2	RMSEV	LVs	RPD	spectral range(nm)
CSR (η_{100})	0.25-0.99	0.18	0.89	0.06	0.82	0.07	11	2.44	900- 2500
viscosity-*K*	2.8-39.1	8.81	0.87	3.0	0.86	3.7	10	2.40	900- 2500
viscosity-n value	0.17-0.49	0.07	0.85	0.03	0.82	0.03	13	2.11	900- 2500
L*	43.9-53.8	2.2	0.6	1.3	0.61	1.4	10	1.54	900- 2500
a*	-(5.2-3.6)	0.4	0.5	0.3	0.51	0.4	8	1.04	900- 2500
b*	7.8-22.9	3.4	0.8	1.6	0.79	1.6	12	2.12	900- 2500
AIS（mg/g DW）	90.9-189.6	18.3	0.79	8.4	0.76	8.9	12	2.05	900- 2500
AIS（mg/g FW）	14.8-33.3	4.1	0.85	1.6	0.84	1.6	12	2.48	900- 2500
DMC (g/g FW)	0.15-0.24	0.02	0.84	0.01	0.84	0.01	12	2.37	900- 2500
SSC (°Brix)	10.3-17.6	2.0	0.82	0.9	0.80	0.9	11	2.16	900- 2500
TA (meq/kg FW)	25.2-109.1	21.6	0.83	8.9	0.80	9.6	11	2.26	900- 2500
glucose (g/kg FW)	13.9-25.7	3.1	0.65	1.8	0.62	2.1	10	1.50	900- 2500
fructose (g/kg FW)	42.1-99.9	15.6	0.71	9.5	0.70	10.0	10	1.56	900- 2500
sucrose (g/kg FW)	33.4-123.1	23.5	0.78	11.0	0.76	11.0	11	2.14	900- 2500
malic (g/kg FW)	2.9-8.3	1.5	0.79	0.7	0.75	0.8	10	1.93	900- 2500