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To cite this version:

Weijie Lan, Benoit Jaillais, Alexandre Leca, Catherine M.G.C. Renard, Sylvie Bureau. A new application of NIR spectroscopy to describe and predict purees quality from the non-destructive apple measurements. Food Chemistry, 2020, 310, pp.125944. 10.1016/j.foodchem.2019.125944 . hal-02992917

HAL Id: hal-02992917

https://hal.inrae.fr/hal-02992917

Submitted on 21 Jul 2022

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Version of Record: https://www.sciencedirect.com/science/article/pii/S0308814619320837
Manuscript_5ed46625a30980191d9245ec6fe2996b

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

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25 **Highlights**

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

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

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

29

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, Symoneaux, Renard, Biau, & Cuvelier, 2012; Espinosa-Muñoz, To, Symoneaux, Renard, 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

69 studies regarding the quality assessment of apple purees have been mainly focused on
70 the changes in polyphenol contents and total antioxidant activity (Loncaric, Dugalic,
71 Mihaljevic, Jakobek, & Pilizota, 2014; Sukhonthara, Kaewka, & Theerakulkait, 2016),
72 color (Oszmiański, Wolniak, Wojdyło, & Wawer, 2008), ascorbic acid (Picouet, Landl,
73 Abadias, Castellari, & Viñas, 2009), organic acids (Bengoechea *et al.*, 1997), sugars
74 (Keenan, Brunton, Butler, Wouters, & Gormley, 2011), polysaccharides (Le
75 Bourvellec, Bouzerzour, Ginies, Regis, Plé, & Renard, 2011), rheological properties
76 (Espinosa-Muñoz, Renard, Symo□eaux, Biau, & Cuvelier, 2013; Espi□osa-Muñoz,
77 Symoneaux, Renard, Biau, & Cuvelier, 2012) and sensory appreciation
78 (Espinosa-Muñoz, To, Symoneaux, Renard, Biau, & Cuvelier, 2011). However,
79 almost all of these quality parameters have been measured through specific laboratory
80 analyses, such as chromatography, which are time-consuming, expensive and not
81 suitable for fast and numerous characterizations. Consequently, the development of
82 rapid, accurate and reliable methods is required to control the quality of the raw
83 apples and processed purees, and meet the ever-increasing demands for consistent and
84 high quality fruit products.
85 Near infrared spectroscopy (NIRS) has been increasingly used for the safety
86 inspection and quality assessment of agricultural products (Nicolai *et al.*, 2007). It has
87 several advantages such as rapid spectrum acquisition, limited preparation
88 requirements and no chemical waste, but it requires an initial calibration step, which
89 is time consuming. Indeed, on a set of samples, representative of the expected
90 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 2nd), and the treatment named Th+ corresponded to 50 to 100 fruits/tree (a

135 standard commercial fruit load) and Th- to 150-200 fruits/tree (highly loaded trees).
136 The 'Golden Smoothee' in 2016 and 'Granny Smith' in 2017 grew under regular fruit
137 thinning (Th-). After harvesting (Golden Smoothee on September 14th, 2016, 'Golden
138 Delicious' on September 11th, 2017 and 'Granny Smith' on September 25th, 2017),
139 apples were kept in a cold storage chamber at 4°C and at around 90% of humidity
140 during one, three and six months (respectively T1, T3 and T6), except the first group
141 (T0) for which apples were analyzed and processed the day after harvest. These
142 storage durations were chosen in order to increase the fruit variability linked to
143 firmness and biochemical changes, such as demethylation and depolymerization of
144 pectins (Billy, Mehinagic, Royer, Renard, Arvisenet, Prost, et al., 2008). Each set (T0,
145 T1, T3 and T6) was divided into two sub-groups. The first one was dedicated for fresh
146 apple characterization and the second one for processing. For characterization, three
147 replicates of 10 apples, representative of the total apple set, were analyzed after one
148 night temperature equilibration at 23°C.
149 First, nondestructive measurements (NIR, color, ethylene releasing rate, fruit weight),
150 and then texture tests (puncture mean load and puncture linear distance) were
151 performed on each apple. After that, each apple was cored and divided as described by
152 Bureau *et al.* (Bureau, Scibisz, Le Bourvellec, & Renard, 2012) in order to create, for
153 each replicate of ten apples, three batches of 40 pieces representative of each apple.
154 The pieces were immediately put in liquid nitrogen to avoid any oxidization. Finally,
155 one batch was stored at -20 °C and then was subsequently freeze-dried to evaluate the
156 alcohol insoluble solids (AIS) contents. The other two batches were stored at -80°C

157 for biochemical characterization measurement.

158 **2.1.2 Purees**

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

169 **2.2 Determination of quality traits**

170 **2.2.1 Color**

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

176 **2.2.2 Ethylene production**

177 Each group of ten apples was put in a hermetic jar at 23°C for 1 hour, and ethylene
178 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 controlled shear rate range 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.

201 **2.2.4 Biochemical characterization of apples and purees**

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

216 **2.3 FT-NIR spectrum acquisition**

217 The spectral data of apples and purees were both acquired with a multi-purpose
218 analyzer spectrometer (Bruker Optics®, Wissembourg, France), which provides
219 diffuse reflectance measurements with a spectral resolution of 2 nm from 800 to 2500
220 nm. For each spectrum, 32 scans were recorded and averaged. The spectral acquisition
221 and instrument adjustments were controlled by OPUS software Version 5.0 (Bruker
222 Optics®). The apples were placed on an automated 30-positions sample wheel, each

223 position corresponding to a measured area of 18 mm diameter. For each intact apple,
224 two spectra were collected (on the blushed and un-blushed sides) though the 18 mm
225 diameter areas at 23°C. Puree were transferred into 10 mL glass vials (5 cm height x
226 18 mm diameter) which were placed on the automated sample wheel of the
227 spectrophotometer. Each puree sample was measured three times on different aliquots.
228 A reference background measurement was automatically activated before each data
229 set acquisition using an internal Spectralon reference.

230 **2.4 Statistical analyses and chemometrics**

231 After ensuring the normal distribution of dataset, the results were presented as mean
232 values and the data dispersion within our experimental dataset expressed as standard
233 deviation values (SD). Analysis of variance (ANOVA) was carried out to determine
234 the significant differences due to the tested factors on both apples and purees using
235 XLSTAT (version 2018.5.52037, Addionsoft SARL, Paris, France) data analysis
236 toolbox. The pairwise comparison between means was performed using Tukey's test
237 at the 95% level of certainty ($p < 0.05$(*), 0.01 (**) and 0.001 (***)). For apples, a
238 one-way ANOVA was applied to access the effect of storage period on 'Golden
239 Smoothee' in 2016 and 'Granny Smith' i□2017; a two-way ANOVA concerned the
240 effects of storage period and fruit thinning on 'Golden Delicious' in 2017. For purees,
241 a two-way ANOVA accessed the effects of storage periods and refining treatments on
242 'Golden Smoothee' and Granny Smith, and a three- way ANOVA for 'Golden
243 Delicious' in terms of fruit thinning, storage periods and puree refining levels.
244 Pearson's determination coefficients (R^2) were calculated in order to study the

245 significance of the relationship between apples and purees and then output as an heat
246 map using R software (version 3.5.2) (R Core Team, 2018) and the additional package
247 named 'ComplexHeatmap' (Gu, Eils, & Schlesner, 2016).
248 Spectral pre-processing and multivariate data analysis were performed with Matlab
249 7.5 (Mathworks Inc. Natick, MA) software using the SAISIR package (Bertrand &
250 Cordella, 2008). All the NIR data were pre-processed with standard normal variate
251 (SNV) and a derivative transform calculation (Savitzky–Golay method, gap size = 11,
252 21, 31, 41) of first or second order. Each of the preprocessing methods was tested in
253 the discrimination models. As SNV pre-processing had the best performances to
254 correct multiplicative interferences and variations in baseline shift, the results shown
255 are those obtained with the SNV pretreatment. Principal Component Analysis (PCA)
256 and Factor Discriminant Analysis (FDA) were carried out on spectral data to evaluate
257 the possibility to discriminate samples according to the tested factors (cultivars,
258 thinning and storage). The specificity and sensitivity values of FDA discriminations,
259 which help for a better evaluation of the rate of sample differentiation, were
260 calculated by the already reported method of Nargis (Nargis *et al.*, 2019). The Partial
261 least-square (PLS) regression method was used to develop predictive models of the
262 quality traits of interest in apples and purees. The whole spectral dataset included 840
263 spectra of apples and 240 spectra of purees. The dataset was randomly split, two third
264 of dataset (560 spectra of apples and 160 spectra of purees) were used for calibration
265 and one third of dataset (280 spectra of apples and 80 spectra of purees) for validation.
266 The procedure was repeated 10 times in order to obtain the suitable dimensions of the

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

272 **3. Results and discussion**

273 **3.1 Apple and puree characteristics measured by classical methods**

274 **3.1.1 Fresh apples**

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

288 During cold storage, mean load, linear distance and AIS content (FW and DW)

289 decreased remarkably ($p < 0.001$) in all apples, indicating an intensive reduction of
290 apple firmness, crunchiness and cell wall material contents (Johnston, Hewett, &
291 Hertog, 2002). Good correlations were observed between AIS and mean load (R^2
292 =0.78 in 'Golden Smoothee', R^2=0.75 in 'Granny Smith', R^2 =0.82 in 'Golden
293 Delicious'). The acidity in all apples decreased significantly with storage ($p < 0.001$)
294 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
295 malic acid. The ethylene production rate increased and then decreased during storage
296 with significant changes ($p < 0.001$). All color parameters (L*, a* and b*) increased
297 clearly for all apples, linked to a degreening and a yellowing during the long-term
298 storage. The changes of all individual sugar contents were significant in 'Golden
299 Smoothee' ($p < 0.05$) and 'Golden Delicious' ($p < 0.001$), but not in 'Granny Smith'
300 ($p > 0.05$). For 'Golden Delicious', SSC and DMC from thinned trees (Th +) appeared
301 to be significantly ($p < 0.001$) higher than from non-thinned trees (Th-).

302 **3.1.2 Apple purees**

303 The fresh apple variability described above affected the characteristics of the
304 corresponding non-refined (NR) purees cooked using the same recipe (**Figure 1c and**
305 **1d**). The NR purees were discriminated according to the apple variety, fruit thinning
306 and storage periods (**Figure 1c**). The first principal component was positively
307 correlated to TA, content of malic acid, AIS (DW and FW) and rheological parameters
308 (η_{100}, K), and negatively linked with colors (L*, b*) and fructose content. The storage
309 periods could be well-classified with this component. The second principal
310 component was highly related to DMC, sucrose content, SSC and AIS content (FW)

311 allowing the separation of varieties and fruit thinning conditions.

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

326 The changes of SSC, sucrose content and DMC in purees were still the major
327 discriminative contributors for apple varieties and fruit thinning conditions during
328 puree processing. Obvious differentiations were observed for SSC and sucrose
329 content between 'Granny Smith' purees and the other purees, in accordance with their
330 changes in raw apples. In 'Golden Delicious', tree thinning (Th+) led to a significant
331 increase ($p < 0.001$) of DMC both in apples and their corresponding processed purees
332 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.

355 Acceptable correlations were also found for SSC (0.79 in NR and 0.81 in Ra), DMC
356 (0.72 in NR and 0.73 in Ra) and malic acid content (0.65 in NR and 0.61 in Ra). For
357 the AIS (DW) contents, good correlations (R^2) were obtained for each variety between
358 raw apples and NR purees (not for Ra purees): 0.76 in 'Golden Smoothee', 0.83 in
359 'Granny Smith' and 0.77 in 'Golden Delicious', but lower when using all NR purees
360 (R^2= 0.65). Moreover, acceptable correlations (R^2> 0.71) were obtained between
361 texture characteristics (mean load and linear distances) of all apples and rheological
362 parameters (η_{100} and *K*) of their corresponding purees, whether non-refined (NR)
363 (**Figure 2a**) or refined (Ra) (**Figure 2b**). The rheological variations in processed
364 purees under the effects of different genotypes, storage periods and refining
365 treatments were consistent with the textural changes in apples. However, no
366 significant correlations (R^2 < 0.44) were found for individual sugars (glucose, sucrose
367 and fructose) between all apples and their purees (NR and Ra), probably because: i)
368 these concentrations changed less during long-term storage than TA and malic acid
369 content, and ii) water content varied during thermal processing and refining
370 treatments.
371 The good correlations of acidity (TA and malic acid content), SSC, DMC and physical
372 properties (textual and rheological parameters) between apples and their purees were
373 in line with PCA results (**Figure 1b and 1d**). The chemical and physical variations in
374 purees were shown to be potentially linked to the raw apple properties.

375 **3.2 Apple and puree characteristics measured by NIRS**

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

388 **3.2.1 Discrimination of fresh apples**

389 The wavelength range with the most variability (between 1700 and 2350 nm),
390 identified by the ANOVA (**Figure 3a**), was chosen to discriminate the effects of
391 cultivar and storage. This range was used to perform PCA and FDA (**Figure 4a and**
392 **4b**).

393 The first PCA displayed the discrimination of apples according to the variety (**Figure**
394 **4a**). The first PC-score (PC1) discriminated 'Granny Smith' (GS) on the left and
395 'Golden Delicious' (GD) and 'Golden Smoothee' (GO) on the right, and accounted for
396 83.5% of the total variability. As observed for the reference data, 'Golden Smoothee'
397 spectra were overlapped with those of 'Golden delicious'. The wavelengths at around

398 1880 nm, 1930 nm and 2100-2300 nm were the main contributors of the PC1 (not
399 shown).The two bands at 1880 nm and 1930 nm are explained by the O-H
400 combinations, which have been reported to characterize the water content in apples
401 (Camps, Guillermin, Mauget, & Bertrand, 2007). The broad band at 2100-2300 nm
402 corresponds to the first combination band of C-H bond of sugars or organic acids,
403 already used to determine the concentration of individual sugars in apple juices (León,
404 Kelly, & Dowey, 2005; Liu, Ying, Yu, & Fu, 2006). These fingerprint wavelengths
405 are consistent with the discrimination of apple cultivars harvested in France (Camps,
406 Guillermin, Mauget, & Bertrand, 2007).
407 In a second step, the different storage periods of all apples could be separated (100%
408 of discrimination sensitivity and specificity between T0 and T1 apples, and 98.5% for
409 sensitivity and 99.5% for specificity between T1 and T3 apples) by FDA (**Figure 4b**).
410 It was observed that T3 and T6 apples were overlapped (**Figure 4b**), in line with their
411 changes of mean load and linear distance (PCA could not well-classified storage
412 periods). However, this result was inconsistent with previous report regarding well
413 classification of storage periods of 'Golden Delicious' at 2°C by FDA (Giovanelli,
414 Sinelli, Beghi, Guidetti, & Casiraghi, 2014). In our experiment, the strong variability
415 and heterogeneity from different apple cultivars and fruit-thinning treatments could
416 provide more variations of water contents and carbohydrates, and thus introduced
417 difficulties to well classify the storage stages after 3 months (T3). The use of different
418 storage temperatures might also be involved, with a faster evolution at 4°C than at
419 2°C. The relevant wavelengths were mainly located in the ranges from 1700-1900 nm

420 and 2250 nm (not shown).

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

424 **3.2.2 Discrimination of apple purees**

425 For purees, the ANOVA indicated major variations in the following wavelength
426 ranges: 800-1050 nm, 1550-1730 nm, 1870 nm and 2100-2200 nm (**Figures 4c and**
427 **4d**). Thus, the whole wavelength range from 800 to 2500 nm was used for FDA on the
428 spectral dataset of all purees (not well-classified with PCA). The first two factors of
429 the FDA allowed the discrimination of the three cultivars, 'Golden Smoothee' (GO),
430 'Granny Smith' (GS) and 'Golden Delicious' (GD), with the discrimination specificity
431 and sensitivity values of 86.8% and 84.6% in GD and GO apples; 84.0% and 82.2%
432 in GD and GS apples; 88.5% and 91.9% in GD and GS apples (**Figure 4c**). The F1
433 and F2 coefficients were both highly correlated with the area between 800 and 1000
434 nm (not shown), which is known as the absorption of apple carbohydrates and water
435 (Giovanelli, Sinelli, Beghi, Guidetti, & Casiraghi, 2014; Zude, Herold, Roger,
436 Bellon-Maurel, & Landahl, 2006), and already used for apple cultivar classification
437 (Bobelyn *et al.*, 2010). Purees could be classified according to the storage periods
438 with a distinct group for T0 and T1 (91.7% of sensitivity and 95.0% of specificity),
439 but a mixed group for T3 and T6 (**Figure 4d**). Besides the aforementioned absorbance
440 region between 800 and 1000 nm, the wavelengths around 1400 nm and between
441 2100 and 2300 nm were also major contributors for discrimination of storage

442 durations. These regions have been shown to be related to water loss and SSC
443 variations, and could be regarded as the fingerprint wavelengths of apple storage
444 periods (Camps, Guillermi□, Mauget, & Bertra□d, 2007; Giova□elli, Si□elli, Beghi,
445 Guidetti, & Casiraghi, 2014; Leó□, Kelly, & Dow□ey, 2005).
446 Other interesting results were obtained with the FDA applied on 'Granny Smith'
447 purees taking into account the refining levels and the storage durations (not shown).
448 According to the F1 and F2 axes, the two refining levels (Na and Ra) were separated
449 both at T0 and T1, but not at T3 and T6. This result is highly consistent with the
450 rheological changes of refined and non-refined purees of 'Granny Smith' (**Suppl.**
451 **Table 2**). This refining treatment led to stronger losses of viscosity and cell wall (AIS)
452 content before the first month of apple storage (T1), compared to purees prepared
453 after three months (T3 and T6).

454 **3.3 Prediction of quality traits by NIRS**

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

460 **3.3.1 Prediction of quality traits by NIRS on fresh apples**

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

464 were further discussed.

465 The prediction results of AIS content (R^2=0.85 expressed in dry weight and R^2=0.83
466 in fresh weight) during cold storage stood out in **Suppl. Table 3**. The prediction of
467 AIS content has already been studied but using the destructive mid-infrared technique
468 on freeze-dried apple powder (Canteri, Renard, Le Bourvellec, & Bureau, 2019), and
469 using NIRS to predict AIS content on 'Golden Delicious' apples during seven months
470 storage at 2 ± 0.5°C with a R^2 of 0.96 (Lovász, Merész, & Salgó, 1994). The lower R^2
471 value in our study was probably in relation with the fact that three varieties and fruit
472 thinning conditions were introduced in the same models. For the crunchiness (linear
473 distance), the prediction result was acceptable (R^2=0.82, RPD=2.34), in accordance
474 with previous results obtained on 'Golden Delicious', 'Braeburn' and 'Fuji' apples
475 during a 7 months cold storage (R^2=0.84), but using the crunchiness data from
476 sensory evaluation and the averaged NIR spectra of each group (Mehinagic *et al.*,
477 2003). Good predictions were obtained with DMC (R^2=0.87, RPD= 2.53) and SSC
478 (R^2=0.81, RPD= 2.21), which were in accordance with previous studies (Giovanelli,
479 Si□elli, Beghi, Guidetti, & Casiraghi, 2014; McGlo□e, Jorda□, Seelye, & Clark, 2003).
480 Moreover, acceptable correlation coefficients were obtained for TA (R^2=0.80, RPD=
481 2.09) and for the main organic malic acid (R^2=0.78, RPD=2.03). For the other
482 individual sugar compounds, results were acceptable for fructose content (R^2=0.81,
483 RPD=1.93) and sucrose content (R^2=0.81, RPD=2.14).

484 Consequently, in apples, NIR spectroscopy was a powerful tool to qualify the
485 crunchiness (linear distance), SSC, TA, DMC, content of individual sugars (fructose

486 and sucrose) and AIS. The benefit of AIS content prediction by NIRS was evident
487 because the classical method of extraction and analysis needs a long time and lots of
488 chemical solvents. Our models were also robust, given the large fruit variability used,
489 with factors such as varieties, thinning practices and cold storage periods.

490 **3.3.2 Prediction of quality traits of all purees**

491 For purees, good predictions were observed for global parameters such as DMC
492 (R^2=0.85, RPD=2.42) and SSC (R^2=0.92, RPD=3.12) (**Suppl. Table 4**). The higher R^2
493 regarding SSC in purees than in apples, could possibly due a better homogeneity of
494 the puree samples after processing. Additionally, acceptable results were also be
495 observed for TA (R^2=0.80, RPD=2.22). For individual compounds, results were
496 acceptable only for fructose (R^2=0.83, RPD=2.51). For the physical properties,
497 rheological parameters (η 100, *K* and n) and color (L*, a* and b*), only poor results
498 were obtained in all purees (R^2 < 0.51). However, in 'Granny Smith' purees (not
499 shown), good correlations were obtained between NIRS and η100 (R^2=0.94,
500 RPD=6.53), and *K* (R^2=0.93, RPD=3.52), and n (R^2=0.87, RPD=2.94). It seemed
501 NIRS provided the possibility to access the evolution of rheological parameters in
502 'Granny Smith' purees from different apple storage times, but this relationship was
503 not robust if a large variability of genotypes and agricultural practices were involved.
504 Moreover, the results were surprising for AIS which was well-predicted in the
505 corresponding intact apples (**Suppl. Table 3**), but not in all processed purees (R^2 <
506 0.69, RPD < 1.59). The acceptable prediction of AIS content in apples probably
507 depended on the good correlation between AIS and textural changes (firmness and

508 crunchiness).

509 **3.3.3 Prediction of puree quality traits from NIR spectra of fresh apples**

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

520 In NR and Ra purees, good predictions were obtained for rheological parameters
521 (η_{100}, K and n). Especially for η_{100}, impressive R^2 and RPD values were observed
522 for NR purees (R^2=0.88, RPD=2.31) and Ra purees (R^2=0.82, RPD=2.44). Good
523 results were also obtained for AIS content (expressed in FW and DW) in NR purees
524 (R^2=0.81, RPD=2.23) and Ra purees (R^2=0.84, RPD=2.48). As the AIS content is one
525 of the main contributors of puree viscosity (Leverrier, Almeida, & Cuvelier, 2016),
526 these concomitant results between AIS content and rheological parameters could
527 probably be related to their good correlations in purees. In all studied purees, good
528 correlations were obtained between their AIS and viscosity behaviors (η_{100}) (R^2
529 =0.75), but not for the AIS and SSC values (R^2=0.32). For coloration, acceptable

530 prediction results of b* value were obtained both in NR purees (R^2=0.81, RPD=2.19)
531 and Ra purees (R^2=0.79, RPD=2.12). Moreover, considering the DMC, SSC and TA,
532 the PLS regression models had a good ability to estimate each characteristic for all
533 purees on the basis of acceptable R^2 and RPD values ($R^2 > 0.80$, RPD > 2.11).
534 However, the NIR technique cannot be used to estimate satisfactorily the content of
535 individual sugars (fructose, sucrose, glucose) and of malic acid of purees depending
536 on the spectral information of raw apples.
537 What stands out in these results was the better predictions of some quality traits of
538 puree from fresh apple spectra (**Table 1 and 2**) than from the puree spectra directly
539 (**Suppl. Table 4**). It was the case for rheological parameters, R^2=0.82 from apples and
540 $R^2 < 0.44$ from purees, possibly owing to the acceptable links ($R^2 > 0.71$) between
541 apple texture (mean load and linear distance) and puree rheological properties (**Figure**
542 **2**). In addition, better PLS results to predict AIS content from fresh apple spectra
543 (R^2=0.81 in FW and 0.84 in DW) were obtained than from purees spectra ($R^2 < 0.69$)
544 (**Suppl. Table 4**), probably due to good relationships between puree viscosity and AIS
545 content mentioned above. Besides, the prediction of DMC, SSC and TA were still
546 acceptable in all cases. Therefore, NIR technique showed a potential to directly
547 predict the viscosity properties, b*, AIS content, SSC, DMC and TA of processed
548 purees using their corresponding apple spectral information directly.
549 Compared with the PLS models used to predict the characteristics of purees based on
550 their own spectra **(Suppl. Tables 3 and 4)**, more LVs and lower prediction accuracy
551 (RPD values) have generally found when models were built using the spectra of the

552 intact apples to predict the characteristics of the processed purees. This fact has been
553 also observed when other raw materials, e.g. meat (Meullenet, Jonville, Grezes, &
554 Owens, 2004) or whole grain (Windham et al., 1997) were used to predict quality
555 traits of the final cooked food. Such indirect prediction is a challenge as the spectra
556 were not acquired on the material for which prediction was done, and because the
557 chemical and textural traits from the material on which the spectra were acquired (the
558 raw apples) are modified by processing. However, such predictions, albeit only
559 semi-quantitative, are relevant for industrial use. Indeed, these developed models
560 provide a promising solution to evaluate puree viscosity, a primary quality trait of this
561 product, and cell wall contents (AIS), only based on spectra of fresh apples. A
562 remarkable fact was that these predictions could not be done using the NIR spectra of
563 the purees themselves (**Suppl. Table 4**).

564 **4. Conclusion**

565 As far as we know, this was the first report concerning the assessment of quality
566 variation of apple purees depending on NIR spectral information of the corresponding
567 raw apples. Up to now, in apple industry, manufacturers use their experience and
568 knowhow to make blend of apples in order to obtain always the same puree. From our
569 results, NIR had the potential to predict internal quality of apples but also that of their
570 processed products: a reliable assessment of texture and taste of the purees could be
571 obtained based only on spectral data of fresh apples. This opens the possibility to sort
572 or select apples according to the expected purees. By systematically scanning all
573 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.

Acknowledgements

The authors thank Patrice Reling, Barbara Gouble, Line Touloumet, Marielle Boge, Caroline Garcia and Gisèle Riqueau (INRA, SQPOV unit) for their technical help. The 'Interfaces' project is an Agropolis Fondation Flashship project publicly funded through the ANR (French Research Agency) under "Investissements d'Avenir" programme (ANR-10-LABX-01-001 Labex Agro, coordinated by Agropolis Fondation). Weijie Lan was supported by a doctoral grant from Chinese Scholarship Council.

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711 **Figure captions**

712 **Figure 1.** Principal Component Analysis of physical, physiological and biochemical
713 compositions for: apples **(a)** and processed NR (no refined) purees **(c)** in three
714 varieties (GO: 'Golden Smoothee' , GD: 'Golden Delicious' and GS: Granny Smith)
715 growing under two different thinning conditions (Th+ marked with red solid circle
716 and Th- with red dotted circle) and stored at 4°C from harvest (T0), 1 (T1), 3 (T3) and
717 6 (T6) months. Correlation plot of the first principal components for apples **(b)** and
718 NR purees **(d)**.

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

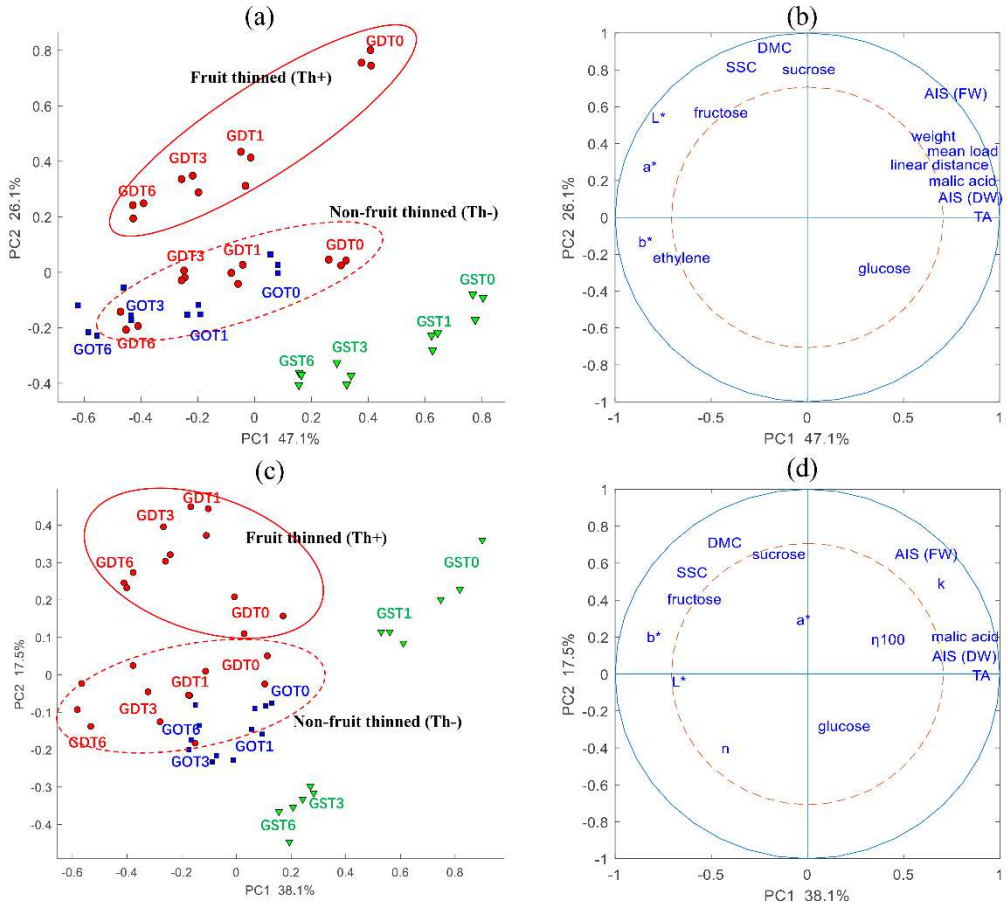
723 **Figure 3.** ANOVA results of the SNV pre-treated NIR spectra between 800 and 2500
724 nm: **(a)** effect of variety o□all apples spectra; **(b)** effect of storage period on all apples
725 spectra; **(c)** effect of variety o□all purees spectra; **(d)** effect of storage period on all
726 purees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

727 **Figure 4.** Factorial maps of the SNV pre-treated NIR spectra of all apples between
728 1700 and 2350 nm or all purees between 800 and 2500 nm: **(a)** Principal Component
729 A□alysis showi□g apples cultivars; **(b)** the Factorial Discriminant Analysis of storage
730 periods of apples; **(c)** Factorial Discriminant Analysis of cultivars of all purees; **(d)**
731 Factorial Discriminant Analysis of storage periods of all purees.

732 'Golden Smoothee' (GO), 'Golden Delicious' (GD), 'Granny Smith' (GS); storage

733 duration at 4°C from harvest (T0), 1 (T1), 3 (T3) and 6 (T6) months.

734 **Figures**



735

736 **Figure 1**

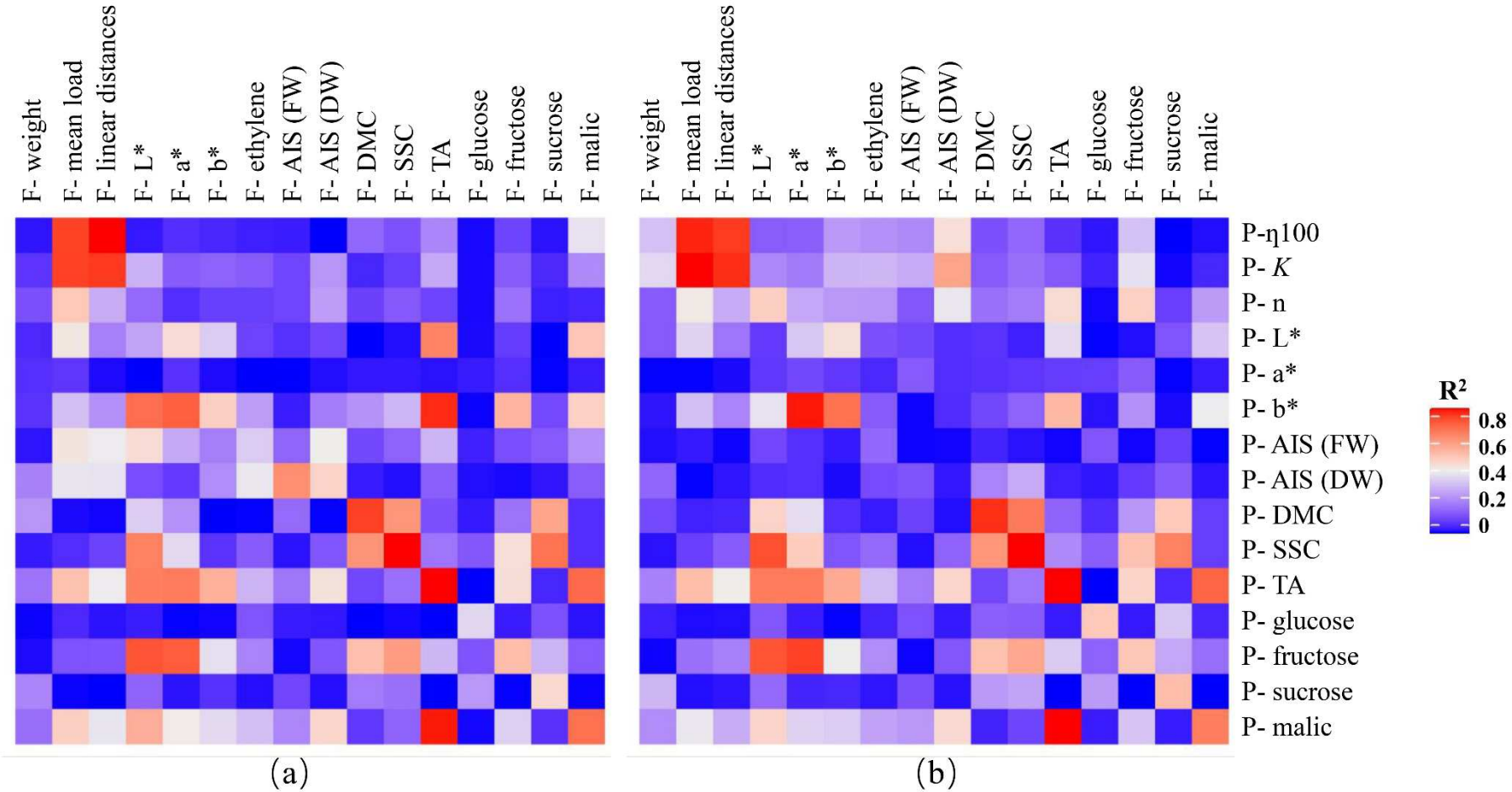

F- weight
F- mean load
F- linear distances
F- L*
F- a*
F- b*
F- ethylene
F- AIS (FW)
F- AIS (DW)
F- DMC
F- SSC
F- TA
F- glucose
F- fructose
F- sucrose
F- malic
P-η100
P- K
P- n
P- L*
P- a*
P- b*
P- AIS (FW)
P- AIS (DW)
P- DMC
P- SSC
P- TA
P- glucose
P- fructose
P- sucrose
P- malic
R²
0.8
0.6
0.4
0.2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

Figure 2

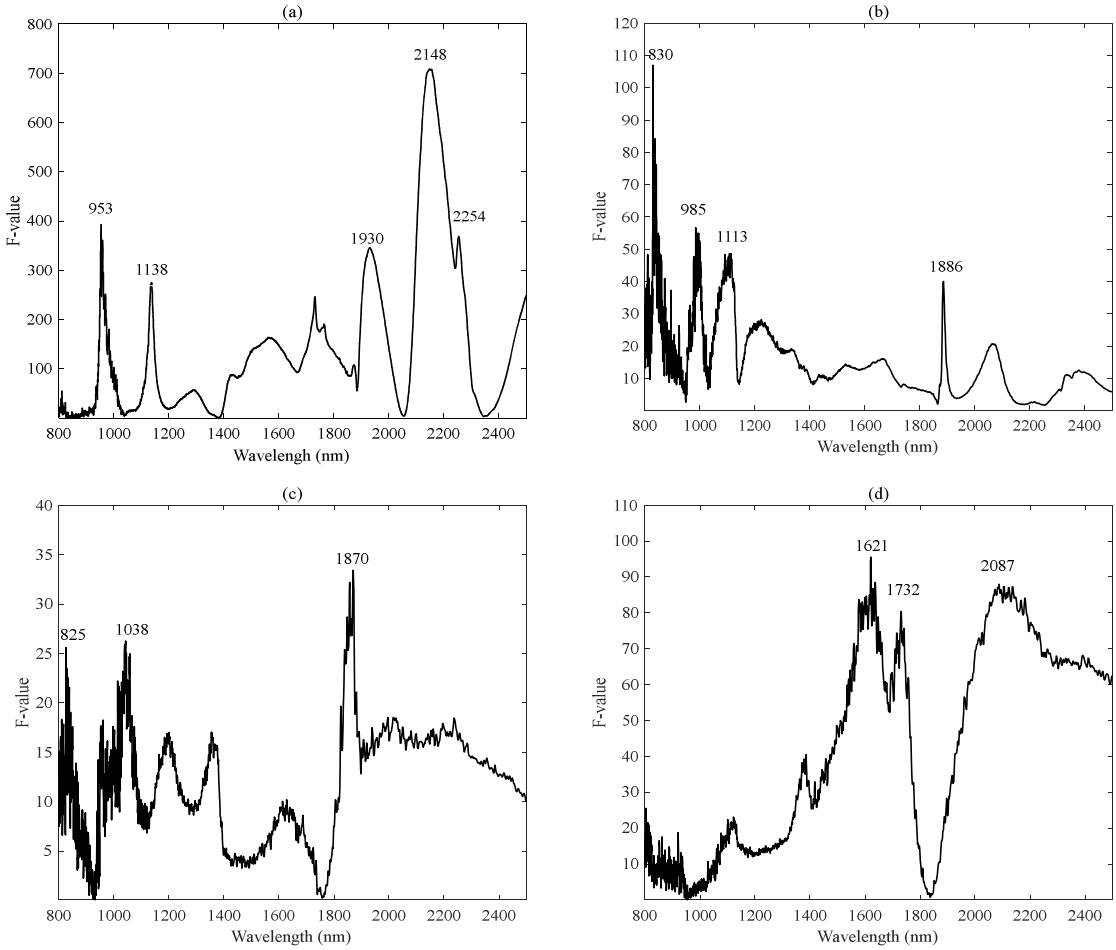
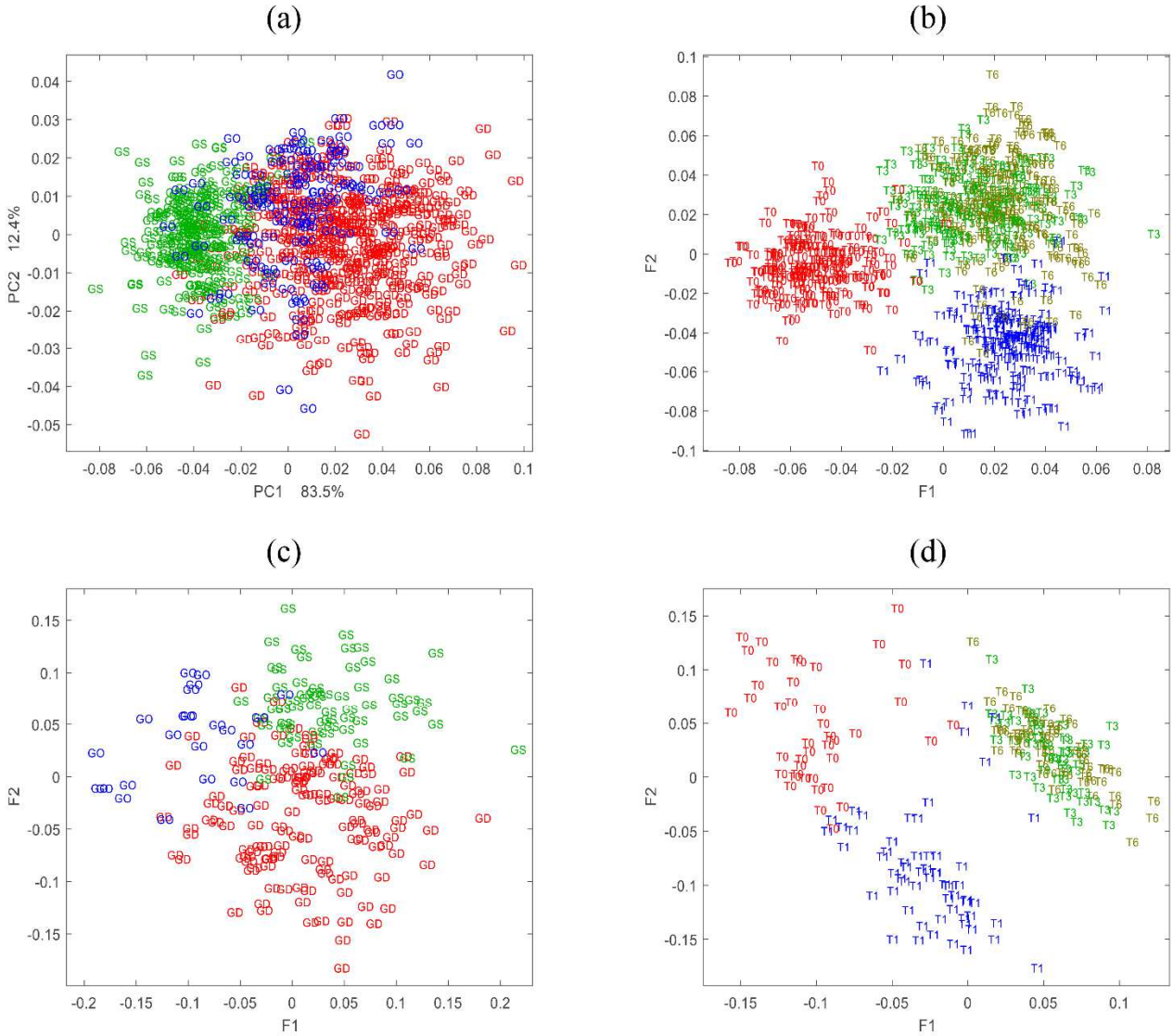

(a)
F-value
Wavelengh (nm)
953
1138
1930
2148
2254
(b)
F-value
Wavelength (nm)
830
985
1113
1886
(c)
F-value
Wavelength (nm)
825
1038
1870
(d)
F-value
Wavelength (nm)
1621
1732
2087

Figure 3



743

744 **Figure 4**

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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

751 **Table 2.** Prediction of puree quality traits from spectral data of fresh apples: PLS (Partial Least Squares) results using NIR spectra of fresh

752 apples from three varieties (‘Granny Smith’, ‘Golden Delicious’ and ‘Golden Smoothee’), two thinning conditions and two harvest seasons, at 4

753 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

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