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Comparison of near-infrared, mid-infrared, Raman spectroscopy and near-infrared hyperspectral imaging to determine chemical, structural and rheological properties of apple purees

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1 **Comparison of near-infrared, mid-infrared, Raman spectroscopy and near-**
2 **infrared hyperspectral imaging to determine chemical, structural and rheological**
3 **properties of apple purees**

4
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34 **Highlights**

35 MIR provided a better discrimination of puree variability than other techniques.

36 MIR gave the best prediction of puree textural and rheological properties.

37 HSI technique had a better ability to assess puree quality and variability than NIR.

38 Raman spectroscopy could not provide sufficient assessment of puree quality.

39 **Abstract**

40 Near-infrared (NIR), mid-infrared (MIR), Raman spectroscopy and hyperspectral
41 imaging (HSI) were comprehensively compared for their capacity to evaluate the
42 composition and texture characteristics of apple purees issued from a large variability
43 (cultivar, fruit thinning, post-harvest mealy texture and processing). NIR, MIR and HSI
44 techniques had a good ability to estimate puree composition such as soluble solids
45 (RPD > 2.5), titratable acidity (RPD > 2.4) and dry matter (RPD > 2.3). Raman
46 spectroscopy was less accurate to determine puree biochemical (RPD < 1.8) and
47 textural parameters (RPD < 1.4) than the other techniques. MIR was the best tool to
48 identify aforementioned factors (> 91.7 % of correct classification) and to satisfactory
49 predict the puree average particle size (RPD = 2.9), viscosity (RPD ≥ 2.1) and
50 viscoelasticity (RPD > 2.3). Consequently, NIR, MIR and HSI should be prioritized as
51 process analytical technologies to detect the variability of purees and assess their
52 texture and taste.

53

54 **Keywords:**

55 *Malus x domestica* Borkh.; Infrared spectroscopy; Raman; Process analytical technique;

56 Puree quality.

57 **1. Introduction**

58 Apple puree is the basic ingredient of many fruit-based products, such as jams,
59 preserves or compotes, yogurts and pie fillings for food industry (Defernez, Kemsley,
60 & Wilson, 1995). It appears to be particularly suitable to test candidate process
61 analytical techniques (PATs) as there are clear levers to introduce controlled variability
62 in a sample set either from raw material or from process conditions (Lan, Jaillais, Leca,
63 Renard, & Bureau, 2020). Today, apple purees are predominantly analyzed by
64 chromatography and specific rheometers to determine their biochemical (Keenan,
65 Brunton, Butler, Wouters, & Gormley, 2011) and rheological properties (Buegy,
66 Rolland-Sabaté, Leca, & Renard, 2020; Espinosa-Muñoz, Renard, Symoneaux, Biau,
67 & Cuvelier, 2013). These methods provide accurate quantifications, but they are time-
68 consuming, expensive and not suitable for fast and numerous characterizations.

69 Developing highly efficient, economic and reliable PATs is a key point for food
70 quality control in industrial and scientific works. Spectroscopic and imaging techniques
71 have been considered to be some of the representative PATs for the rapid qualification
72 of agricultural commodities and processed food (Cullen, O'Donnell, & Fagan, 2014).
73 In particular, near-infrared (NIR), mid-infrared (MIR), Raman and hyperspectral
74 imaging (HSI) offer the advantages of a minimal sample preparation and a rapid data
75 acquisition.

76 NIR technique has been widely applied for the safety inspection and quality
77 assessment of apple fruits at the wavelength range from 780-2500 nm (Nicolai, et al.,
78 2007; Pissard, et al., 2013). The broad bands of NIR contain the overlapping absorption

79 bands corresponding mainly to overtones and combinations of vibrational mode C-H
80 and O-H bonds of fruit components (Osborne, 2006). Several internal attributes of apple
81 purees, such as soluble solids content (SSC), dry matter content (DMC) and titratable
82 acidity (TA), can thus be evaluated from a single spectrum, with acceptable precisions
83 (Lan, Jaillais, Leca, Renard, & Bureau, 2020).

84 MIR spectroscopy on fresh and processed apples gives a good estimation of SSC,
85 DMC, TA, malic acid and some individual sugars (Bureau, et al., 2013; Lan, Renard,
86 Jaillais, Leca, & Bureau, 2020). Compared to the low structural selectivity in the broad
87 bands of NIR spectra, more resolved fundamental bands of MIR spectra allow to better
88 elucidating the chemical and structural information of samples. However, the lower
89 energy of MIR radiations and the strong water interactions in fruit suspensions prevent
90 the sensitive evaluation of chemical compositions and structural properties (Lan,
91 Renard, et al., 2020).

92 Raman spectroscopy can provide a complementary interpretation of molecule
93 vibration changes in polarizability, which is distinct from the vibration used in MIR by
94 the changes in dipole moment (Pistorius, 1996). For highly hydrated products, such as
95 fresh and processed fruits, Raman presents two advantages in comparison with infrared:
96 a weak scattering of the polar O-H group and more intense bands of homo-nuclear
97 molecular bonds (C-C, C=C, etc.). To date, no detailed study has compared the
98 differences and limitations of Raman and infrared spectroscopy (NIR and MIR) to
99 determine the structural and rheological properties of fruit purees.

100 Hyperspectral imaging (HSI) is an emerging platform technique that integrates

101 imaging and spectroscopy to provide both spatial and spectral information (Baeten &
102 Dardenne, 2005). Several applications of HSI were carried out on fresh fruits to
103 estimate their external and internal quality (Baeten & Dardenne, 2005; Mendoza et al.,
104 2011; Ma et al., 2018). For fruit processed purees, no work has been done on HSI to
105 detect their biochemical composition, structural and rheological properties.

106 To date, the comprehensive comparison of these techniques to determine chemical
107 (SSC, TA, DMC, individual sugars and malic acid), structural (particle sizes) and
108 rheological (viscosity and viscoelasticity) characteristics of fruit puree products stays
109 limited. Therefore, identifying the most efficient spectroscopic method to assess quality
110 of processed fruit purees is a crucial point to prioritize further developments.

111 In this work, four different spectroscopic and imaging techniques, namely NIR,
112 MIR, Raman and HSI, were applied on the same set of diverse (cultivar, fruit thinning
113 practice, fruit texture, processing) apple puree samples in order to: i) evaluate their
114 potential to detect the puree variability; ii) compare their performance to predict
115 chemical, structural and rheological characteristics of purees and then iii) identify
116 signals specific of the puree properties.

117 **2. Materials and methods**

118 **2.1 Apple purees**

119 2.1.1 Apples

120 A large variability of apples has been introduced in this work, in order to explore
121 the potential of different spectroscopic techniques to detect the variability of the

122 processed apple purees. Around 50 kg of Apples of four cultivars: ‘Golden Delicious’
123 (GD), ‘Granny Smith’ (GS), ‘Royal Gala’ (GA) and ‘Braeburn’ (BR, BM) were
124 harvested at a commercial maturity in 2018 from the La Pugère Experimental Orchard
125 (Chambre d’Agriculture des Bouches du Rhône) (Mallemort, Bouches du Rhône,
126 France).

127 Fruit thinning generates significant differences of apple cell numbers during
128 growth ([Link, 2000](#)), and results in intensive variations of puree structural and chemical
129 properties ([Buergy, Rolland-Sabaté, Leca, & Renard, 2020](#); [Lan, Jaillais, et al., 2020](#)).
130 In this study, GS, GA, BR, BM and half of GD apples were grown under a standard
131 chemical fruit thinning practice (Th+) with 50-100 fruits / tree. The other half of GD
132 apples was non-thinned (Th-) with 150-200 fruits / tree.

133 After harvesting, different storage conditions (temperature, time, humidity etc.) can
134 strongly influence apple physical, structural, and biochemical properties ([Tu et al.,](#)
135 [2000](#)). Four apple groups (GD Th+, GD Th-, GS, GA) were stored at 4 °C in normal
136 atmosphere to ensure starch regression (customised phytotron, Froid et Mesures,
137 Beaucouzé, France). As post-harvest storage is known to particularly affect the texture
138 of Braeburn apples ([Tu et al., 2000](#)), two different storage conditions were applied
139 specifically on Braeburn apples, resulting either in crunchy Braeburn apples (BR;
140 stored at 4 °C in normal atmosphere), or mealy Braeburn apples (BM; kept for 11 days
141 at 23 °C and at around 90% relative humidity).

142 Totally, six apple groups (GD Th-, GD Th+, GS, GA, BR and BM) were used for
143 puree processing (**Fig. 1**).

144 2.1.2 Purees processing

145 For all apple groups, three replicates of apple purees were processed from 3 kg of
146 apples each. After sorting and washing, apples (3 kg) were cored, and sliced into 12
147 portions, then processed under vacuum by a multi-functional processing system
148 (RoboQbo Qb8-3, Bentivoglio, Italy), following two different processing recipes:

149 - I) ground at 3000 rpm for 202 s during the increase of temperature and heated at
150 70 °C for 15 min, then pasteurized at 95 °C for 2 min;

151 -II) ground at 3000 rpm for 360 s during the temperature increase step, followed
152 by 400 rpm at 95 °C for 17 min.

153 Afterwards, half of each processed puree was refined at 0.5 mm using a Robot
154 Coupe C80 automatic refiner (Robot Coupe C80, Robot Coupe SNC, Vincennes,
155 France) and the other was not refined. Finally, all processed apple purees were
156 conditioned in hermetically sealed cans, then cooled at 23 °C before the measurements
157 performed the day after. In total, 72 puree samples (6 apple groups × 2 processing
158 recipes × 2 refining levels × 3 processing replicates) were obtained (**Fig. 1**).

159 **2.2 Determination of quality traits**

160 2.2.1 Rheological and structural analyses

161 The puree rheological measurements, consisting in rotational (flow curve) and
162 oscillatory (amplitude sweep) tests, were carried out using a Physica MCR-301
163 controlled stress rheometer (Anton Paar, Graz, Austria) equipped with a vane measuring
164 system with a 3.46 mm gap (CC27/S cup and FL100/6W bob, Anton Paar), at 22.5 °C.

165 The flow curves were performed after a pre-shearing period of 1 minute at 50 s^{-1}
166 followed by 5 minutes at rest. The viscosity was then measured at a controlled shear
167 rate range of $[10; 250] \text{ s}^{-1}$ on a logarithmic ramp, at a rate of 1 point every 15 seconds.
168 The complete flow curves were fitted with a power law model according to the previous
169 works (Lan, Jaillais, et al., 2020), as described by Eq. (1).

$$170 \quad \eta = K \dot{\gamma}^{n-1} \quad (\text{Eq1})$$

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

173 Amplitude sweep tests were performed at an angular frequency of 10 rad.s^{-1} in the
174 deformation range of $[0.01; 100]\%$, in order to determine the linear viscoelastic range
175 of the purees and the yield stress, defined as the crossing point between the storage
176 modulus (G') and the loss modulus (G'') curves. The damping factor $\tan \delta = G''/G'$
177 of purees was calculated.

178 The particle sizes were measured according to our previous work (Lan, Jaillais, et
179 al., 2020). Puree samples were diluted in distilled water to separate particles and stained
180 with calcofluor white at 0.1 g/L and highlighted with a 365 nm UV lamp. A high-
181 resolution digital video camera (Baumer VCXU31C, Baumer SAS, Fillinges, France)
182 with a macro lens (VSTech 0513, VS Technology Corporation, Tokyo, Japan.) was used
183 to visualize the distribution and dispersion of puree particles. The particle sizes
184 averaged over volume $d(4:3)$ (de Brouckere mean) and over surface area $d(3:2)$ (Sauter
185 mean) were measured with a laser granulometer (Mastersizer 2000, Malvern
186 Instruments, Malvern, UK).

187 2.2.2 Biochemical analyses

188 Several biochemical analyses were performed on apple purees based on the
189 previous works (Bureau et al., 2013; Lan, Jaillais, et al., 2021). SSC was determined
190 with a digital refractometer (PR-101 ATAGO, Norfolk, VA, USA) and expressed
191 in °Brix at 23 °C. TA was determined by titration up to pH 8.1 with 0.1 mol/L NaOH
192 and expressed in mmol H⁺/kg of fresh weight (FW) using an autotitrator (Methrom,
193 Herisau, Switzerland). Individual sugars and malic acid were quantified using
194 colorimetric enzymatic kits, according to the manufacturer's instructions (R-biopharm,
195 Darmstadt, Germany). The content of glucose, fructose, sucrose and malic acid were
196 expressed in g/kg of FW. These measurements were performed with a SAFAS flx-
197 Xenius XM spectrofluorimeter (SAFAS, Monaco) at 570 nm for sugars and 450 nm for
198 malic acid. DMC was estimated from the weight of freeze-dried samples upon reaching
199 a constant weight (freeze-drying for 5 days). Cell wall materials (AIS) of purees were
200 isolated using the alcohol insoluble solids method proposed by Renard (2005) and the
201 cell wall contents (AIS contents) were expressed in FW.

202 2.3 Spectral and image data acquisition

203 2.3.1 NIR spectroscopy

204 NIR spectra were collected with a multi-purpose analyzer (MPA) spectrometer
205 (Bruker Optics®, Wissembourg, France) at 23 °C. Puree samples were transferred into
206 10 mL glass vials (5 cm height × 18 mm diameter) which were placed on the
207 automated sample wheel of the spectrophotometer. Logarithmic transformed

208 reflectance spectra ($\log(1/R)$) were acquired with a spectral resolution of 8 cm^{-1} from
209 12500 to 4000 cm^{-1} (corresponding to wavelengths from 800 to 2500 nm). Each
210 spectrum corresponded to the average of 32 scans. The spectral acquisition and
211 instrument adjustments were controlled by OPUS software Version 5.0 (Bruker
212 Optics®, Ettlingen, Germany). A reference background measurement was
213 automatically acquired before each data set acquisition using an internal Spectralon
214 reference. Each puree sample was measured randomly three times on different aliquots.
215 The mean of three replicate scans for each sample was calculated, and finally 72 NIR
216 spectra of different apple purees (6 apple groups \times 2 processing recipes \times 2 refining
217 levels \times 3 processing replicates) were used in subsequent chemometric analysis.

218 2.3.2 MIR spectroscopy

219 MIR spectra of purees were acquired at $23\text{ }^{\circ}\text{C}$ using a Tensor 27 FTIR spectrometer
220 (Bruker Optics®, Wissembourg, France) equipped with a horizontal attenuated total
221 reflectance (ATR) sampling accessory and a deuterated triglycine sulphate (DTGS)
222 detector. The purees were placed at the surface of a zinc selenide (ATR-ZnSe) crystal
223 with six internal reflections. Spectra with 32 scans each were collected from 4000 cm^{-1}
224 to 800 cm^{-1} with a 4 cm^{-1} resolution and were corrected against the background
225 spectrum of air. Three replications of spectral measurement were performed randomly
226 on each puree, and these averaged MIR spectra of the 72 samples were used for further
227 analysis.

228 2.3.3 Raman spectroscopy

229 Raman spectra were acquired on a Confocal Raman Microscope Senterra II
230 spectrometer (Bruker Optics, Ettlingen, Germany) with a 785 nm diode laser and a
231 thermoelectrically cooled CCD detector, operating at -65 °C. For spectra collection,
232 each puree sample was manually placed and compacted in 36 holes (those in the middle)
233 of a 96 well aluminium plate (12 × 8) with an inner diameter of 6 mm each. After
234 removing the water of purees by evaporation at the ambient temperature (~20 °C),
235 spectra were accumulated with a bleaching of 20 s, an integration time of 2 s and 7
236 coadditions using a 100 mW laser. Raman intensity were recorded from 50 to 3650 cm⁻¹
237 with a spectral resolution of 4 cm⁻¹ intervals. OPUS 7.8 Software (Bruker Optics,
238 Ettlingen, Germany) was used for spectral data acquisition. Each sample was
239 independently and randomly scanned six times. The final spectrum of each puree was
240 the average of these 6 replicates, resulting in 72 Raman spectra.

241 2.3.4 HSI acquisition

242 The hyperspectral images of apple purees were acquired on a pushbroom (a line-
243 scanning type) near infrared hyperspectral imaging system (SPECIM, Oulu, Finland),
244 which consisted of a SWIR camera (SWIR-CL-400-N25E, SPECIM) covering the
245 spectral range of 900-2500 nm with a spectral resolution of about 12 nm, an OLES 56
246 camera lens (SPECIM), an illumination source (halogen lamps) and a translating
247 scanner. Before measurements, the reflectance calibration was performed based on our
248 previous work (Lan, Jaillais, et al., 2021). All the image acquisition parameters
249 (exposure time of camera, scanning speed etc.) were controlled by the LUMO®
250 software from SPECIM. Each puree sample was placed on a hole (with an inner

251 diameter of 3 cm) of the standard white plate (nine holes totally). All images were
252 acquired in the reflectance mode and the final image size for each kernel is 387×127
253 $\times 288$, the two first values representing pixel dimensions in the x and y directions (field
254 of view of 9.5×3.1 cm, with a spatial resolution of $245 \mu\text{m}$) and the third value
255 accounting for the number of spectral channels. As the beginning and ending
256 wavelengths contained noise caused by the instrument itself, the 258 bands from 990
257 to 2450 nm were selected for further spectral analysis. The averaged HSI spectrum of
258 each puree sample was calculated and finally 72 HSI spectra were used for further
259 discrimination and regression analyses.

260 **2.4 Statistical analyses of reference data**

261 After checking for normal distribution with a Shapiro-Wilk test ($\alpha=0.05$), the
262 reference data of processed purees are presented as mean values and the data dispersion
263 within our experimental dataset expressed as standard deviation values (SD) (**Table S1**).
264 Analysis of variance (ANOVA) was carried out to determine the significant differences
265 due to the different apple cultivars, process recipes and mechanical refining treatments
266 (**Table S1**) using XLSTAT (version 2018.5.52037, Addinsoft SARL, Paris, France) data
267 analysis toolbox. Principal component analysis (PCA) was carried out on all reference
268 data of processed purees to evaluate their discriminant contributions using Matlab 7.5
269 software using the SAISIR package ([Cordella & Bertrand, 2014](#)).

270 **2.5 Chemometric analysis**

271 NIR, MIR, Raman and HSI spectra were pre-processed with Matlab 7.5 software
272 using the SAISIR package (Cordella & Bertrand, 2014). The discriminant analysis and
273 multivariate regression were performed with several packages of the R software
274 (version 4.0.2) (R Core Team, 2019), as detailed in our previous work (Lan, Bureau, et
275 al., 2021).

276 Several different preprocessing methods have been performed on NIR, MIR,
277 Raman and HSI spectral metrics. Particularly, smoothing (Savitzky Golay algorithm
278 with a window size of 3, 13, 23 variables) referred to the numerical operations on puree
279 spectra in order to reduce the noise. Standard normal variate (SNV) performed a
280 normalization of all puree spectra that consists in subtracting each spectrum by its own
281 mean and dividing it by its own standard deviation. Savitzky-Golay derivatives (the first
282 or second derivatives with gap sizes of 11, 21, 31, 41) were used to resolve overlapping
283 puree spectral signals and enhance signal properties. All these methods and their
284 combinations (smoothing + SNV, SNV + first derivation, SNV + second derivation,
285 smoothing + SNV + first derivation, smoothing + SNV + second derivation, as well as
286 the direct processing of the raw spectra) were used to pretreat the spectra for
287 discrimination and regression, to compare and obtain the best results.

288 After several pretests, smoothing (Savitzky Golay algorithm with a window size of
289 13 variables) with SNV transformed NIR data in 800-2500 nm; the SNV pre-processed
290 MIR spectra in 1800-900 cm^{-1} ; the smoothing with SNV (a window size of 13 variables)
291 of Raman in 1800-800 cm^{-1} and the SNV with 3 windows (a window size of 3 variables)

292 smoothed HSI data in 990-2450 nm had the best performances to classify and assess
293 the puree quality and were retained for further analysis.

294 Partial least squares (PLS) regression, a typical linear algorithm, combines
295 principal component analysis and canonical correlation analysis (Geladi & Kowalski,
296 1986). In short, PLS models maximize the covariance between Y- matrix (reference
297 datasets) and X- matrix (spectra dataset) in a way to have better predictions of Y- matrix
298 by maximizing the variance of X-matrix. It has been successfully used to determine the
299 global quality parameters of apple purees using NIRS information (Lan, Jaillais, Leca,
300 Renard, & Bureau, 2020).

301 Random forest (RF) is an ensemble of learning methods for classification,
302 regression and other tasks that operates by constructing a multitude of decision trees at
303 training time (Ho, 1995). For classification tasks, the output of RF is to identify a class
304 selected by most trees. For regression tasks, the mean or average prediction of
305 individual trees is returned.

306 Support vector machine (SVM) has been introduced for predicting numerical
307 property values. SVM can efficiently perform a non-linear classification using what is
308 called the ‘kernel trick’, implicitly mapping their inputs into high-dimensional feature
309 spaces. Besides, SVM regression models can resolve nonlinear relationships in original
310 feature spaces through dimensionality extension (Noble, 2006).

311 These two machine learning approaches (RF and SVM) have been specially
312 constructed to address large and complex nonlinear systems (Liu, Wang, Wang & Li,
313 2013) and have provided satisfactory estimation of puree rheological properties (Lan,

314 [Bureau, et al., 2021](#)). In this study, PLS, SVM and RF algorithms were used to
315 discriminate purees (**Part 3.2**) and predict their quality traits (**Part 3.3**). The 10-fold
316 full cross-validation was applied to the 72 spectra of NIR, MIR, Raman and HSI
317 datasets, respectively.

318 For discrimination models (PLS-DA, SVM-DA and RF-DA), the discrimination
319 accuracy (acc) was used to describe the discriminating ability of the different
320 spectroscopic techniques (**Table 2** and **Table 3**). The ability of the four different
321 techniques coupled with PLS-DA, SVM-DA and RF-DA was compared to classify
322 different factors: (a) cultivars (48 purees from (Th+) GD, GA, GS and BR apples), (b)
323 process recipes (72 samples of processes I and II), (c) refining treatments (72 NR and
324 Ra), (d) fruit thinning practices (24 GD purees from Th+ and Th-) and (e) fruit stress
325 treatments (24 Braeburn purees with crunchy BR and mealy BM). The main vibrational
326 bands observed in NIR, MIR, Raman and HSI datasets, which contributed to the best
327 discrimination models are shown for all factors (a-e) (**Table 3**).

328 Prediction of puree rheological (K , n , G' , G'' , yield stress and $\tan \delta$), structural
329 (d4:3 and d3:2) and biochemical properties (SSC, DMC, TA, malic acid, fructose,
330 glucose, sucrose, AIS) were compared according to the four spectroscopic techniques
331 (NIR, MIR, Raman and HSI) (**Tables 4** and **5**). For regression models (PLS-R, SVM-
332 R and RF-R), the prediction performances were assessed by the determination
333 coefficient of cross-validation (R_{cv}^2), the root mean square error of cross-validation
334 ($RMSE_{cv}$) and the residual predictive deviation (RPD). Particularly, the RPD values
335 from 2 to 2.5 indicate the possibility for approximate qualitative predictions, whereas
336 from 2.5 to 3 or above correspond to good and excellent prediction accuracy ([Nicolai,
337 et al., 2007](#)). The optimal numbers of latent variables (LVs) were obtained from
338 developed PLS-DA and PLS-R models. Besides, the main attributed vibrational bands

339 were selected based on the beta-coefficients of PLS models (Lan, Bureau, et al., 2021),
340 and the variable importance (VIP) of SVM and RF models using the ‘varImp’ function
341 by ‘caret’ package in R software (Kuhn, 2015). Particularly, the VIP method here was
342 based on the mean square error of developed models using all the spectral variables
343 (MSE_0) and the mean square error of new models (MSE_n) by permuting each spectral
344 variable. Afterwards, the VIP score for each spectral variable was calculated by the
345 increase of mean square error (IncMSE), following Eq (1):

$$346 \quad IncMSE = \left(\frac{MSE_n - MSE_0}{MSE_0} \right) * 100\% \quad (1)$$

347 A larger *IncMSE* indicates a greater importance for a spectral variable. The main
348 correlated spectral signals of the best developed models are shown in **Tables 3, 4** and
349 **5**.

350 **3 Results and discussion**

351 **3.1 Characteristics of apple purees**

352 After puree processing, the different purees provided a large variability of chemical,
353 textural and rheological properties (**Table S1**). In the PCA, the first principal
354 component (PC1) and the second principal component (PC2) explained respectively
355 48.6% and 19.5% of the total variance. This PCA allowed to mainly represent the strong
356 differences due to apple cultivars taking into account all the characterized parameters
357 of the total 72 different purees after processing (**Fig. 2**).

358 ‘Granny Smith’ (GS) purees (C) were clearly discriminated from the other puree
359 groups along the PC1. The GS purees presented a significantly ($p < 0.001$) higher
360 viscosity (K and n) and elasticity (yield stress, G' and G''), particle size $d(4:3)$ and
361 volume $d(3:2)$, TA, malic acid and AIS content than the others (**Fig. 2b** and **Table S1**).

362 Remarkable higher values ($p < 0.001$) for SSC and DMC allowed the separation of

363 ‘Golden Delicious’ (A and B) and ‘Royal Gala’ purees (D) along the second principal
364 component (**Fig. 2a** and **2b**). Thinning practice (Th+) on GD apples (B) resulted in a
365 less viscous purees than non-thinned GD purees (A) (**Table S1**), which is in line with
366 our previous research (Lan, Renard, et al., 2020). For all non-refined (NR) purees,
367 ‘Royal Gala’ had the lowest viscoelastic moduli ($G' < 934.0 \pm 35.4$ Pa, $G'' < 194.3 \pm$
368 7.2 Pa), titratable acidity ($TA < 3.8 \pm 0.2$ meq/kg) and cell wall contents ($AIS < 128.4$
369 ± 9.5 mg/g). However, the overlapping of the two kinds of ‘Braeburn’ purees (E and F)
370 (**Fig. 2a**) revealed the difficulty to produce different purees after processing and
371 refining of either, crunchy (puncture linear distance of 14.0 ± 1.2 Newton) and mealy
372 (puncture linear distance of 11.7 ± 0.7 Newton) apples.

373 The two different processing recipes used here (Processes I and II) led to significant
374 ($p < 0.01$) changes of puree rheological behaviors (K , n , G' , G'' , yield stress and $\tan \delta$)
375 and particle distributions (d4:3 and d3:2), but not of chemical attributes (SSC, DMC
376 and AIS; $p > 0.05$) (**Table S1**). Particularly, purees processed at 95 °C and 400 rpm
377 (Process II) had a soft solid-like behavior. They were more viscous (K and n) with
378 higher G' and G'' and larger particles (d4:3 and d3:2) than the purees processed at 70 °C
379 and 3000 rpm (Process I).

380 Moreover, as expected, the refining treatment generated a significant ($p < 0.01$)
381 decrease of puree viscosity and elasticity (K , n , G' , G'' and yield point), particle sizes
382 (d4:3 and d3:2) and cell wall contents, but did not impact ($p > 0.05$) chemical attributes.

383 **3.2 Discrimination of variability of apple purees**

384 Generally, PLS-DA models developed using NIR, MIR, Raman and HSI spectra of
385 purees had the best performances to discriminate the cultivars (a), processes (b), fruit
386 thinning (d) and stress treatments (e) (**Table 2**). However, specifically for refined purees,
387 MIR technique coupled with machine learning (RF-DA and SVM-DA) gave a higher
388 discrimination accuracy (acc > 90.3%) of purees than PLS-DA (acc = 84.7%) (**Table**
389 **2**).

390 NIR technique coupled with PLS-DA models gave a correct discrimination of the
391 four cultivars (acc = 88.8%, 4 LVs), the two GD fruit thinning purees (acc = 86.7%, 2
392 LVs) and the two Braeburn storage impacts (acc = 95.8%, 3 LVs). The specific NIR
393 spectral regions at 818-850, 1849, 1880 and 2145-2155 nm mainly contributed to
394 cultivar discrimination (**Table 3**). Particularly, the spectral area at 800-1000 nm, which
395 is known as the absorption of apple carbohydrates and water variations ([Giovanelli,](#)
396 [Sinelli, Beghi, Guidetti, & Casiraghi, 2014;](#) [Zude, Herold, Roger, Bellon-Maurel, &](#)
397 [Landahl, 2006](#)), has been used for the apple cultivar classification ([Bobelyn, et al.,](#)
398 [2010](#)). The absorption bands around 1880 nm are explained by the O-H combinations
399 of water contents in apples ([Camps, Guillermin, Mauget, & Bertrand, 2017](#)). The broad
400 band at 2100-2200 nm corresponds to the first combination band of C-H bonds of
401 sugars and acids, and has already been highlighted in our previous work ([Lan, Jaillais,](#)
402 [et al., 2020](#)). Besides, the wavelengths around 1400 nm (1345, 1392 and 1379-1384
403 nm), related to the soluble solids variations in apple juices ([Kaur, Künnemeyer, &](#)
404 [McGlone, 2020](#)), were one of the major contributors for the discriminations of apple
405 thinning (Th+ and Th-) and stress treatments (crunchy BR and mealy BM). However,

406 NIR technique was not able to well classify (acc < 55.6%) the processing recipes and
407 refining levels, which nevertheless induced intensive structural and rheological
408 variations of purees (**Table S1** and **Table 3**).

409 MIR technique provided a better discrimination of all studied factors (**Table S-2**)
410 than NIR. Particularly, three different discrimination models (PLS-DA, SVM-DA, RF-
411 DA) (**Table 2**) allowed to classify the four puree cultivars with the acc values of 100%.
412 The specific spectral wavenumbers at 1723-1718, 1107, 1061 and 1022 cm^{-1} (**Table 3**),
413 attributed to the stretching bonds of C=O of malic acid, and the C-O and C-C of glucose,
414 fructose and sucrose (Bureau, Cozzolino, & Clark, 2019), were consistent with the
415 measured differences of purees coming from different cultivars (**Fig. 2** and **Table S-2**).
416 Compared to NIR results, the satisfactory classifications by MIR of processing recipe
417 (acc = 100 %) and refining (acc = 91.7%) were mainly based on the overlapped region
418 between 1750 and 1650 cm^{-1} (1749 cm^{-1} , 1730-1715 cm^{-1} and 1640-1628 cm^{-1} in **Table**
419 **3**), related to the organic acids, soluble polysaccharides, pectins, phenolics and
420 absorbed water (Lan, Renard, et al., 2020). MIR was able to highlight the
421 physicochemical modifications of apple purees generated by different processing
422 strategies (heating temperature and grinding speed) and mechanical refining treatments.
423 Besides the aforementioned spectral signals, the excellent PLS discriminations of apple
424 thinning (acc = 100%) and stress treatments (acc = 100%) were linked to three specific
425 wavenumbers at 1084, 1056 and 998 cm^{-1} , corresponding to the variations of glucose
426 and sucrose in fruits (Bureau, et al., 2019).

427 For Raman spectroscopy, PLS-DA models developed over the range of 800-1800

428 cm^{-1} had a lower discrimination accuracy and more LVs to discriminate puree cultivars
429 ($\text{acc} = 81.3\%$, 7 LVs), thinning practices ($\text{acc} = 75.0\%$, 6 LVs) and stress treatments
430 ($\text{acc} = 70.8\%$, 6 LVs) than the models obtained with NIR and MIR (**Table 3**). The main
431 vibrational bands responsible for these discriminations were related to the variations of
432 major sugars and acids in apple purees, which have been highlighted in honey products
433 (Pompeu, et al., 2018) and soft drinks (Ilaslan, Boyaci, & Topcu, 2015). In particular,
434 were observed the C-C stretching and C-H deformation vibrations of glucose at 840-
435 842 cm^{-1} (Özbalci, Boyaci, Topcu, Kadilar, & Tamer, 2013); the stretching of C-O-C at
436 872 cm^{-1} and the deformation of C-OH of fructose at 872, 939, 944 and 1054 cm^{-1}
437 (Cerchiaro, Sant'Ana, Temperini, & da Costa Ferreira, 2005; Mathlouthi & Luu, 1980;
438 Özbalci, et al., 2013); the C-O and C-OH vibrations of sucrose at 1126 cm^{-1} (Ilaslan, et
439 al., 2015; Pierna, Abbas, Dardenne, & Baeten, 2011) and the C=O stretching of malic
440 acid at 1734 cm^{-1} (Barańska, Kuduk-Jaworska, Szostak, & Romaniewska, 2003).
441 Interestingly, Raman spectra discriminated different puree processing conditions with
442 the acc value of 82.3%. Besides the aforementioned wavenumbers, the specific Raman
443 bands at 845 and $1433\text{-}1436 \text{ cm}^{-1}$ were observed to discriminate puree processing
444 changes. These wavenumbers are known to represent the C-O-C and COO-
445 antisymmetric stretching of pectins during the clarification of apple juice (Camerlingo,
446 et al., 2007).

447 HSI technique coupled with PLS-DA showed a relatively higher discrimination
448 accuracy of puree cultivars ($\text{acc} = 100\%$, 7 LVs), processing recipes ($\text{acc} = 86.1\%$, 10
449 LVs), fruit thinning practices ($\text{acc} = 91.6\%$, 6 LVs) and stress treatments ($\text{acc} = 100\%$,

450 4 LVs) than the conventional NIR spectroscopy, but using a higher number of latent
451 variables. Besides the similar aforementioned wavenumber regions as in NIR around
452 1400, 1880 and 2100-2300 nm, specific spectral areas at 1048-1088 and 1106-1145 nm
453 were observed, corresponding to the SSC and DMC variations in fruits (Lan, Jaillais,
454 et al., 2021; Wang, Peng, Xie, Bao, & He, 2015). Comparing to NIR, PLS-DA on the
455 averaged HSI puree spectra gave an impressive improvement of the discrimination of
456 puree processing recipes, from 51.4% to 86.1%. However, both NIR and HSI spectra
457 had a limited ability to discriminate the different refining levels (< 58.3% correct
458 identification). These two techniques had the potential to detect puree variability
459 (cultivar, fruit thinning, process) involving significant differences in composition
460 (Table S-1), but not to estimate puree textural changes (refining) (Table S-1).

461 3.3 Prediction of apple puree quality traits

462 According to the RPD values described by Nicolai et al. (2007), NIR showed a
463 poor prediction ($R_{cv}^2 < 0.52$, RPD < 1.4) of puree rheological (K , n , G' , G'' , yield stress
464 and $\tan \delta$) and structural parameters (d4:3 and d3:2) (Table 4). However, it gave a good
465 prediction of puree composition, such as DMC ($R_{cv}^2 = 0.82$, RPD = 2.3), SSC ($R_{cv}^2 =$
466 0.83 , RPD = 2.5), TA ($R_{cv}^2 = 0.83$, RPD = 2.4) and pH ($R_{cv}^2 = 0.85$, RPD = 2.6).
467 Particularly, the specific wavebands in the intervals 937-1050, 1180-1210 and 1290-
468 1330 nm, corresponding to O-H and C-H vibrations of water and carbohydrates
469 (Giovanelli, et al., 2014; Zude, et al., 2006), highly contributed to the DMC and SSC
470 models,. Besides the aforementioned absorbance regions, NIR wavenumbers between
471 2208 and 2254 nm, corresponding to the combination bands of C-H and O-H (Wang, et

472 [al., 2015](#)), were also considered in the puree DMC prediction. The wavelengths located
473 around 1600 nm (1534-1607 nm for TA models) and 1850 nm (1835-1873 nm for TA
474 and pH models) were used to estimate puree acidity, already described to correspond to
475 the C-O vibration of COOH and O-H combinations ([Camps, et al., 2017](#); [Wang, et al.,](#)
476 [2015](#)). The prediction of puree individual compounds was acceptable only for malic
477 acid ($R_{cv}^2 = 0.80$, RPD = 2.1). Generally, NIR spectra coupled with PLS gave a better
478 estimation of puree quality than SVM and RF regression.

479 MIR technique was potentially able to estimate the rheological parameters (K , n ,
480 G' , G'' and $\tan \delta$) with acceptable R_{cv}^2 (> 0.81) and RPD (> 2.0) values (**Table 4**).
481 Particularly, PLS and RF models obtained acceptable predictions of the consistency (K)
482 ($R_{cv}^2 > 0.81$, RPD > 2.1) and flow (n) ($R_{cv}^2 > 0.80$, RPD > 2.0) parameters of the power-
483 law viscosity model of apple purees. PLS models gave the best predictions ($R_{cv}^2 > 0.82$,
484 RPD > 2.3) of the viscoelastic parameters G' and G'' of purees but were less accurate
485 for the yield stress ($R_{cv}^2 = 0.77$, RPD = 1.7). Impressively, MIRS coupled with PLS
486 showed an excellent prediction of $\tan \delta$ ($R_{cv}^2 = 0.96$, RPD = 5.1), corresponding to the
487 integrative assessment of both elastic and viscous contributions of apple purees
488 ([Espinosa-Muñoz, et al., 2013](#)). The spectral region at 1500-1750 cm^{-1} was highly
489 relevant to estimate puree viscosity and viscoelasticity. It corresponds to the C=O and
490 C-O stretching of carboxylic acids at 1745-1740 cm^{-1} and the C=O vibration of pectic
491 methyl ester at 1628-1634 cm^{-1} ([Liu, Renard, Rolland-Sabaté, Bureau, & Le Bourvellec,](#)
492 [2020](#)). Concerning the puree structural properties, RF model was the best to predict
493 particle sizes over volume $d(4:3)$ ($R_{cv}^2 = 0.88$, RPD = 2.9) and over surface area $d(3:2)$

494 ($R_{cv}^2 = 0.82$, RPD = 2.2). For composition, acceptable to good PLS predictions were
495 obtained for SSC, DMC, TA, pH, malic acid and sucrose, giving RPD from 2.2 to 3.9
496 (**Table 5**). The specific spectral signals related to the acids at 1736-1718 cm^{-1} and to the
497 fructose and sucrose at 1065-1055 cm^{-1} and 1024-1016 cm^{-1} (Bureau, et al., 2019), were
498 the major contributors of SSC and DMC models. The excellent predictions of TA and
499 pH, with RPD values of 3.6 and 3.9, respectively, depended on the particularly strong
500 absorptions bands between 1736-1715 cm^{-1} . However, a lower RPD (RPD = 2.2) and a
501 higher LVs were obtained for malic acid than for TA. For individual sugars, an
502 acceptable PLS prediction was obtained for fructose ($R_{cv}^2 = 0.85$, RPD = 2.6) based on
503 its typical fingerprints at 1155, 1056 and 980 cm^{-1} (Bureau, et al., 2019; Lan, Renard,
504 et al., 2020), but neither for sucrose ($R_{cv}^2 < 0.78$, RPD <1.9) nor for glucose ($R_{cv}^2 <$
505 0.49, RPD <1.4).

506 Raman spectroscopy showed a limited ability to estimate the rheological and
507 structural properties of apple purees with low R_{cv}^2 (< 0.48) and RPD (< 1.4) values
508 (**Table 4**). These results were in line with the lower ability of the aforementioned Raman
509 model to distinguish between non-refined and refined purees (acc = 56.9%) (**Part 3.2**).
510 Moreover, none of the developed Raman models gave acceptable predictions of the
511 global (SSC, DMC, TA and pH) and individual biochemical compositions (sugars, acids
512 and cell wall contents) of apple purees. The best Raman model had a R_{cv}^2 of 0.71 and
513 a RPD value of 1.8, indicating a possible application only to distinguish puree samples
514 presenting a large variation of titratable acidity (TA).

515 The models based on HSI data could not predict rheological (K , n , G' , G'' , yield
516 stress, $\tan \delta$) ($R_{cv}^2 < 0.48$, $RPD < 1.4$) and structural (d4:3 and d3:2) ($R_{cv}^2 < 0.47$, RPD
517 < 1.4) properties. Acceptable PLS predictions were obtained for SSC ($R_{cv}^2 = 0.86$, RPD
518 $= 2.7$), DMC ($R_{cv}^2 = 0.84$, $RPD = 2.4$), TA ($R_{cv}^2 = 0.83$, $RPD = 2.4$) and pH ($R_{cv}^2 =$
519 0.85 , $RPD = 2.6$). Particularly, the most contributing wavelengths, located at around
520 1180-1219, 1282-1327 and 2179-2207 nm, were the same as described with the NIR
521 spectroscopy (**Table 5**). However, none of the models could predict individual sugars
522 (fructose, glucose and sucrose) ($R_{cv}^2 < 0.74$, $RPD < 1.8$) and AIS contents ($R_{cv}^2 < 0.42$,
523 $RPD < 1.3$).

524 **3.4 Comparison of NIR, MIR, Raman and HSI performances**

525 NIR spectroscopy, the easiest to apply and cheapest spectroscopic techniques in
526 this work, showed an acceptable ability ($2.3 < RPD < 2.6$) to predict puree major
527 chemical composition, including SSC, DMC, TA and pH. Such good NIR predictions
528 will probably contribute to the development of the rapid routine evaluation of the
529 composition of fruit-based products. For individual components, a good estimation was
530 only obtained for malic acid, depending on its positive correlation with TA ($R^2 = 0.78$)
531 and pH ($R^2 = 0.76$). However, NIR could not provide acceptable estimations of puree
532 textural changes, in line with our previous conclusions ([Lan, Jaillais, et al., 2020](#)).

533 Compared to NIR, MIR technique had the potential to assess puree rheological
534 properties, including both, viscosity and viscoelasticity. However, the predictions
535 shown in this paper were less accurate ($RPD > 2.0$) than our previous ones ($RPD > 2.4$),
536 which concerned purees presenting a larger range of rheological behaviors ([Lan, Jaillais,](#)

537 [et al., 2020](#)). Interestingly, among puree viscoelastic parameters, $\tan \delta$ was the best
538 estimated by MIR (RPD = 5.1). Compared to machine learning models (SVM and RF),
539 PLS regressions generally showed a better ability to predict puree rheological and
540 biochemical properties. However, for the puree particle structure (size and volume), RF
541 regression provided the best predictions. The informative wavenumber regions at 1500-
542 1750 and 900-1200 cm^{-1} should be considered for rheological and structural
543 assessments of apple purees, which was in line with previous works ([Ayvaz, et al., 2016](#);
544 [Lan, Renard, et al., 2020](#)). MIR coupled with PLS regression provided the best
545 prediction of the global quality traits of purees (SSC, DMC, TA and pH) with the
546 possibility to evaluate some individual components (malic acid and sucrose). The lower
547 prediction of malic acid than of TA was probably due to its relatively low concentration
548 (3.0 - 7.5 g/kg of malic acid and 3.5 – 11.1 g/kg of TA) and limited variations (SD =
549 1.0 g/kg of malic acid, SD = 2.2 g/kg of TA). For individual sugars, the higher internal
550 correlations between fructose and SSC ($R^2 = 0.78$) than between sucrose and SSC (R^2
551 = 0.51) probably explained the better prediction of fructose than of sucrose.

552 In this study, Raman spectroscopy showed a potential to discriminate different
553 purees, according to cultivar and processing recipe (acc > 81.3%), but it was not able
554 to predict puree rheological, structural and chemical parameters. However, Raman
555 gives excellent biochemical predictions on homogeneous samples, such as commercial
556 tomato purees ([Baranska, et al., 2006](#)) and honey products ([Özbalci, et al., 2013](#); [Pierna,](#)
557 [et al., 2011](#)). It has also been used to detect the rheological changes of monotonous
558 mixed food matrices ([Nawrocka, Miś, & Szymańska-Chargot, 2016](#); [Ngarize, Adams,](#)

559 & Howell, 2004). In this work, the unsatisfactory predictions using Raman
560 spectroscopy could be due to i) the very weak spectral signals corresponding to the
561 biochemical variations in apple purees (even after water evaporation before spectrum
562 acquisition) and ii) the variable heterogeneity according to the puree refining and
563 grinding, which make a barrier against an efficient light diffusion.

564 The models based on the averaged NIR-HSI spectra of apple purees provided a
565 significant improvement of puree discrimination (**Table 3**) and a slight increase in
566 quality prediction (**Table 4 and Table 5**) in comparison with the results issued from a
567 measurement of a limited sample area ($\sim 2 \text{ cm}^2$) by NIR spectroscopy. The averaged
568 NIR-HSI spectra, which contained a richer spectral information of puree heterogeneity
569 than the local NIR spectra, might explain the better model performance and relative
570 higher numbers of LVs (Cheng & Sun, 2017). However, both NIR spectroscopy and
571 HSI technique had a limited ability to detect puree differences after refining and to
572 predict their rheological and structural properties. Strangely, the PLS-DA models using
573 the full number of HSI spectra of each puree had a relatively lower discriminating
574 accuracy than their corresponding averaged spectra. Previous works noticed the
575 heterogeneity of tested samples usually affected the NIR and HSI determination
576 precisions (Prieto, Roehe, Lavín, Batten, & Andrés, 2009). The large heterogeneity,
577 including irregular particle size and shape and the high water content on puree surface,
578 could introduce a strong diffuse reflection and spectral noise during the HSI image
579 acquisition. Although NIR-HSI on purees slightly improved the prediction of SSC and
580 DMC over the NIR results, the much larger volume of dataset and the longer time

581 needed for image pre-processing limited its use in comparison with NIR local
582 measurements.

583 Further, the AIS, which contributes to the rheological properties of processed puree
584 products, was not well evaluated in this study whichever the spectroscopic technique
585 or chemometric method used directly on puree samples.

586 **4. Conclusion**

587 This study provided a first comprehensive assessment to choose the best technique
588 among NIR, MIR, Raman spectroscopies and HSI for evaluating apple puree variability
589 and quality. MIR had the best performance to provide an accurate identification of puree
590 properties due to apple variability (cultivar, fruit thinning and postharvest stress) and
591 processing conditions (heating, grinding and refining). It gave also a reliable evaluation
592 of puree rheological and structural characteristics and composition (RPD values from
593 2.1 to 5.1). NIR and HSI techniques can be more easily adapted to routine
594 characterization of the more global parameters in purees (soluble solids, titratable
595 acidity and dry matter), but not of their textural changes. Raman spectroscopy offered
596 an insufficient information to evaluate apple puree variability and quality. Clearly,
597 Raman spectroscopy should not be prioritized in further studies on the characterization
598 of apple purees.

599 The current study also enables considering future applications with NIR, NIR-HSI
600 and MIR according to the industrial or research needs (speed of data acquisition and
601 presentation of the sample). These techniques are very suitable for the development of

602 Process Analytical Technology in order to trace samples and optimize conditions during
603 processing.

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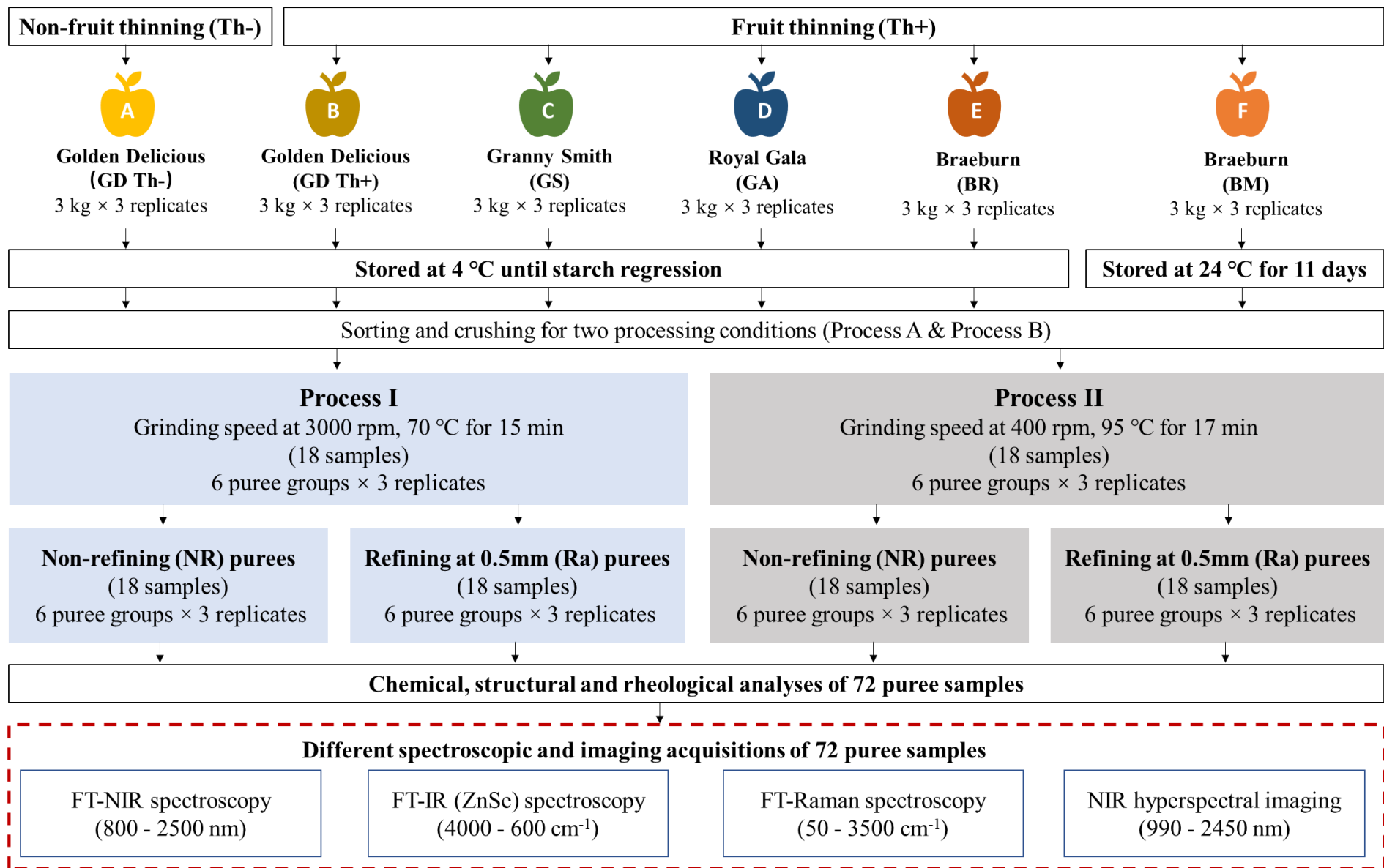
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768 **Figure captions**

769 **Fig. 1.** Experimental scheme of apple puree processing, quality characterization and
770 spectral acquisition.

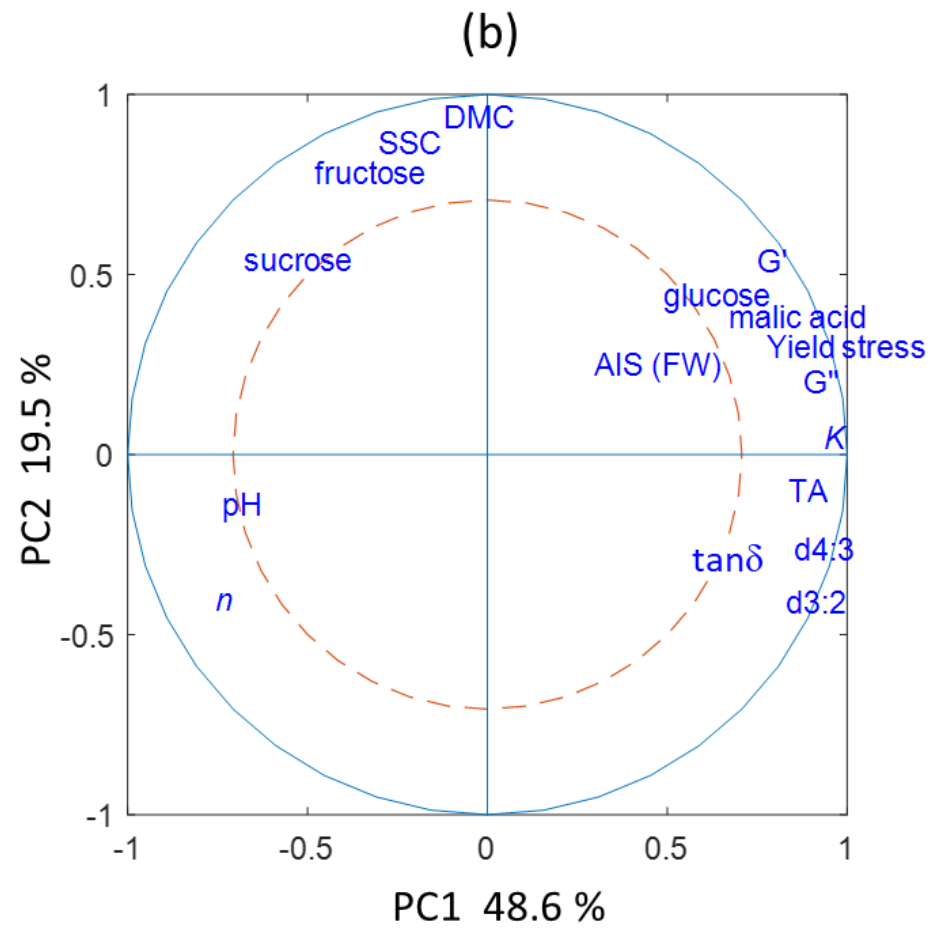
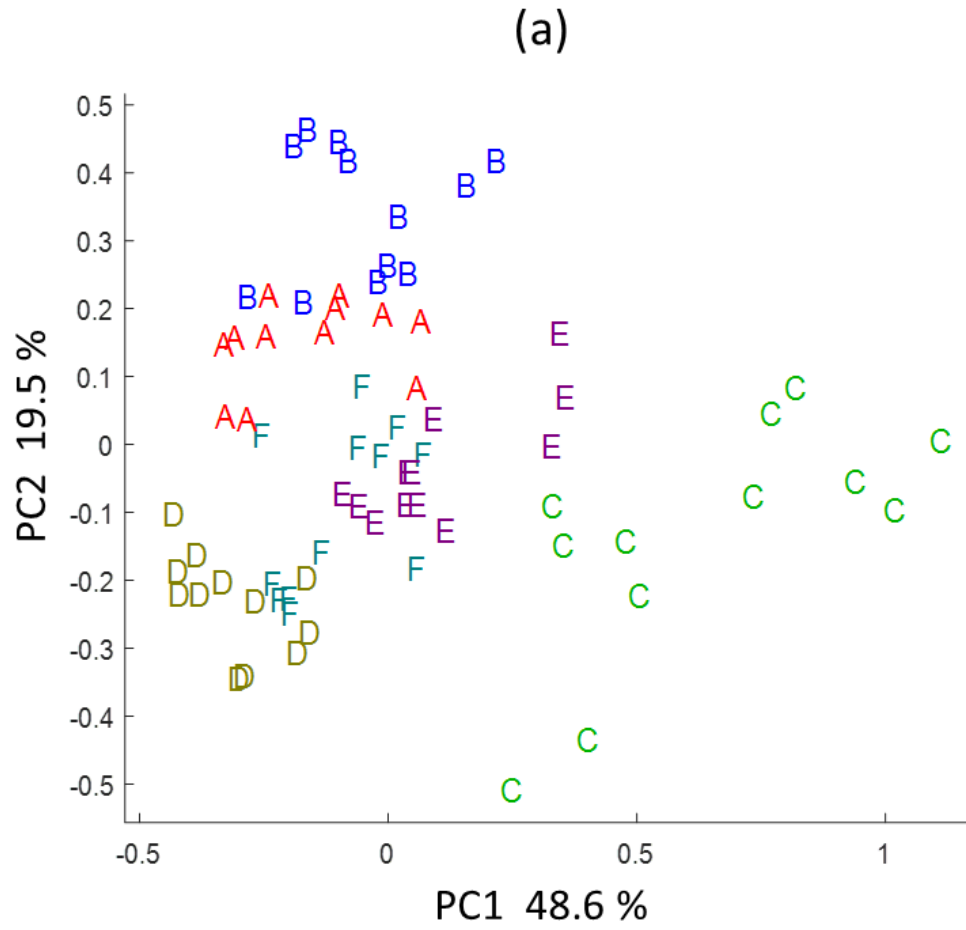
771 **Fig. 2.** Principal component analysis on chemical, structural and rheological parameters
772 of six puree groups (A: GD Th-; B: GD Th+; C: GS; D: GA; E: BR; F:BM): **(a)** the
773 scores plot of the two first components (PC1 and PC2); **(b)** the correlation plot of the
774 PC1 and PC2.



775

776

Fig. 1



777

778 **Fig. 2**

Table 1. The common names and their abbreviations used in this study

Common names	Abbreviations
process analytical techniques	PATs
near infrared spectroscopy	NIR
mid infrared spectroscopy	MIR
Raman spectroscopy	Raman
hyperspectral imaging	HSI
‘Golden Delicious’	GD
‘Granny Smith’	GS
‘Royal Gala’	GA
Crunchy ‘Braeburn’ stored at 4 °C	BR
Mealy ‘Braeburn’ stored at 23 °C	BM
fruit thinned / non-thinned apples	Th+ / Th-
non-refined / refined	NR / Ra
partial least square	PLS
random forest	RF
support vector machine	SVM
the storage modulus of purees	G’
the loss modulus of purees	G’’
G''/G' of purees	$\tan \delta$
puree particle sizes averaged over volume	d4:3
puree particle sizes averaged over surface areas	d3:2
dry matter content	DMC
soluble solid content	SSC
titratable acidity	TA
alcohol insoluble solids	AIS
standard deviation value	SD
principal component analysis	PCA
fresh weight	FW
standard normal variate	SNV
determination coefficient of cross validation	R_{cv}^2
root mean square error of cross validation	RMSEP
the number of latent variables	LVs
residual predictive deviation	RPD

781 **Table 2.** Discrimination using 10-fold full cross-validation PLS-DA, SVM-DA and RF-DA models of apple purees according to (a) cultivars, (b) processes, (c)
 782 refining levels, (d) fruit thinning practices of Golden Delicious apples, (e) stress treatments of Braeburn apples, using NIR, MIR, Raman and HSI data.

Spectral techniques	NIR			MIR			Raman			HSI		
	800- 2500 nm			900- 1800 cm ⁻¹			800- 1800 cm ⁻¹			990-2450 nm		
	PLS-DA	SVM-DA	RF-DA	PLS-DA	SVM-DA	RF-DA	PLS-DA	SVM-DA	RF-DA	PLS-DA	SVM-DA	RF-DA
(a) Cultivar (GD/GS/BR/GA)												
No. of samples	48	48	48	48	48	48	48	48	48	48	48	48
Correct discrimination rate	88.8 %	81.25 %	84.6 %	100.0 %	100.0 %	100.0 %	81.3 %	50.0 %	60.4 %	100 %	72.9 %	72.9 %
LVs	4	-	-	3	-	-	7	-	-	7		
(b) Process (I/ II)												
No. of samples	72	72	72	72	72	72	72	72	72	72	72	72
Correct discrimination rate	51.4 %	31.9 %	44.4 %	100 %	97.2 %	93.1 %	82.3 %	67.7 %	67.7 %	86.1 %	41.7 %	47.2 %
LVs	4	-	-	5	-	-	8	-	-	10		
(c) Refining levels (NR/ Ra)												
No. of samples	72	72	72	72	72	72	72	72	72	72	72	72
Correct discrimination rate	51.4 %	38.9 %	55.6 %	84.7 %	90.3 %	91.7 %	56.9 %	40.3 %	45.8 %	55.1 %	51.4 %	58.3 %
LVs	5	-	-	4	-	-	7	-	-	6		
(d) Fruit thinning (Th+/ Th-)												
No. of samples	24	24	24	24	24	24	24	24	24	24	24	24
Correct discrimination rate	86.7 %	53.3 %	82.5 %	100.0 %	100.0 %	100.0 %	75.0 %	16.7 %	45.8 %	91.6 %	79.2 %	87.5 %
LVs	3	-	-	3	-	-	6	-	-	6		
(e) stress treatments (BR/ BM)												
No. of samples	24	24	24	24	24	24	24	24	24	24	24	24
Correct discrimination rate	95.8 %	63.3 %	87.5 %	100.0 %	100.0 %	100.0 %	70.8 %	25.0 %	54.2 %	100.0 %	58.3 %	87.5 %
LVs	3	-	-	3	-	-	6	-	-	4		

783 Note: ‘Cultivar’: (four varieties of ‘Golden Delicious’, ‘Braeburn’, ‘Granny Smith’ and ‘Royal Gala’); ‘fruit thinning’: different fruit thinning practices for Golden Delicious apples (50

784 - 100 fruits/ tree or 150-200 fruits/ tree); ‘stress’: two different textures of Braeburn apples (11 days at 24 °C or 2 months at 4 °C); ‘processing’: two processing recipes (70 °C for 15

785 mins with 3000 rpm grinding or 95 °C for 17 mins with 400 rpm grinding); 'refining': two refining conditions after puree processing (refined at 0.5 mm or not refined).

Table 3. The main attributions for vibrational bands of the best overall discrimination models developed for puree samples.

Spectra	Spectral ranges	Factors	No. samples	Model	LVs	acc (%)	Key frequencies
							NIR (nm), MIR (cm ⁻¹), Raman (cm ⁻¹), HSI (nm)
NIR	800-2500 nm	cultivar	48	PLS-DA	5	88.8	818-850, 1849, 1880, 2145-2155
		process	72	PLS-DA	4	51.4	/
		refining	72	RF-DA	-	55.6	/
		fruit thinning	24	PLS-DA	2	86.7	904, 1392, 1864
		stress	24	PLS-DA	3	95.8	913, 1345, 1379-1384
MIR	1800- 900 cm ⁻¹	cultivar	48	PLS-DA	4	100.0	1723-1718, 1107, 1061, 1022
		process	72	PLS-DA	5	100.0	1730-1715, 1640-1628, 1138, 1084, 1001-998
		refining	72	RF-DA	-	91.7	1749, 1636, 1061, 1018, 995
		fruit thinning	24	PLS-DA	3	100.0	1772, 1593, 1084, 1022, 998
		stress	24	PLS-DA	3	100.0	1658-1608, 1056, 1018, 1001
Raman	800-1800 cm ⁻¹	cultivar	48	PLS-DA	7	81.3	842, 873, 1064, 1126, 1266, 1433, 1610
		process	72	PLS-DA	8	82.3	816-818, 845, 939, 972, 1362-1367, 1433-1436, 1734
		refining	72	PLS-DA	7	56.9	/
		fruit thinning	24	PLS-DA	6	75.0	842, 1054, 1077, 1427, 1608, 1675
		stress	24	PLS-DA	6	70.8	840, 904, 944, 1059-1063, 1334, 1734
HSI	990-2450 nm	cultivar	48	PLS-DA	7	100.0	1106-1145, 1259, 1338, 1406, 1869-1874, 1931-1964
		process	72	PLS-DA	10	86.1	1048-1088, 1191, 1242, 2117, 2274-2387, 2437
		refining	72	RF-DA	/	58.3	/
		fruit thinning	24	PLS-DA	6	91.6	1065-1088, 1338-1367, 2145, 2331-2342, 2376-2398, 2426
		stress	24	PLS-DA	4	100.0	1048, 1134, 1389, 1947, 2409

Note: acc: discrimination accuracy; PLS-DA: partial least square discrimination; RF-DA: random forest discrimination. ‘Cultivar’: four apple varieties of ‘Golden Delicious’, ‘Braeburn’,

‘Granny Smith’ and ‘Royal Gala’ ; ‘fruit thinning’: different fruit thinning practices for Golden Delicious apples (50 - 100 fruits/ tree or 150-200 fruits/ tree); ‘stress’: two stress

treatments of Braeburn apples (11 days at 24 °C or 2 months at 4 °C); ‘processing’: two processing recipes (70 °C for 15 mins with 3000 rpm grinding or 95 °C for 17 mins with 400

790 rpm grinding); 'refining': two refining conditions after puree processing (refined at 0.5 mm or not refined).

791 **Table 4.** Prediction of rheological and structural properties of apple purees using the full cross-validation PLS, SVM and RF regression based on their NIR, MIR,
 792 Raman and HSI spectra.

Parameter	Spectra	Ranges	SD	PLS-R				SVM-R			RF-R			Key frequencies
				R _{cv} ²	RMSE _{CV}	RPD	LVs	R _{cv} ²	RMSE _{CV}	RPD	R _{cv} ²	RMSE _{CV}	RPD	NIR (nm), MIR (cm ⁻¹), Raman (cm ⁻¹), HSI (nm)
Viscosity- <i>K</i>	NIR	6.6 - 46.8	8.7	0.41	6.8	1.3	6	0.31	8.2	1.1	0.32	7.7	1.1	/
	MIR			0.81	4.1	2.1	7	0.71	5.5	1.6	0.81	4.1	2.1	1712, 1682 - 1668, 1539, 1152, 1094, 1061, 998
	Raman			0.37	6.95	1.3	6	0.31	7.4	1.3	0.31	7.2	1.2	/
	HSI			0.54	6.1	1.4	10	0.27	7.5	1.2	0.36	6.6	1.3	/
Viscosity- <i>n</i>	NIR	0.19 - 0.34	0.04	0.52	0.03	1.4	6	0.30	0.04	1.0	0.35	0.03	1.2	/
	MIR			0.81	0.02	2.2	8	0.80	0.02	2.1	0.80	0.02	2.1	1745 - 1740, 1712 - 1710, 1539, 1140, 1081, 1065-1059,1036, 980
	Raman			0.48	0.03	1.4	8	0.36	0.03	1.4	0.44	0.03	1.3	/
	HSI			0.42	0.03	1.3	7	0.25	0.03	1.1	0.33	0.03	1.2	/
G' (Pa)	NIR	617 - 1962	322	0.32	270	1.2	6	0.11	320	1.0	0.27	282	1.1	/
	MIR			0.82	140	2.3	8	0.80	156	2.1	0.83	139	2.3	1745-1740, 1707, 1634, 1558 - 1537, 1140, 1078, 1063, 1036, 980
	Raman			0.10	326	1.0	6	0.11	303	1.0	0.25	276	1.2	/
	HSI			0.38	263	1.2	9	0.21	298	1.1	0.26	273	1.2	/
G'' (Pa)	NIR	114 - 593	92	0.36	77	1.2	6	0.21	92	1.0	0.26	84	1.1	/
	MIR			0.84	36	2.5	6	0.77	62	1.5	0.81	42	2.2	1745-1740, 1709, 1634-1628, 1558 - 1537, 1139, 1065, 1034, 980
	Raman			0.12	100	0.9	6	0.22	82	0.9	0.20	82	1.1	/
	HSI			0.41	74	1.3	10	0.16	84	1.1	0.19	85	1.1	/
yield stress	NIR	6.4 - 27.7	5.2	0.36	4.2	1.2	6	0.21	5.2	1.0	0.34	4.5	1.2	/
	MIR			0.77	3.0	1.7	7	0.73	2.8	1.8	0.67	3.0	1.8	/
	Raman			0.33	4.3	1.2	8	0.26	4.5	1.2	0.27	4.4	1.2	/
	HSI			0.47	4.0	1.3	11	0.27	4.4	1.2	0.36	4.3	1.2	/
tan δ	NIR	0.18 - 0.30	0.03	0.22	0.03	1.1	5	0.16	0.03	1.0	0.15	0.03	1.0	/
	MIR			0.96	0.01	5.1	7	0.95	0.01	3.7	0.96	0.01	4.5	1749, 1537, 1109 - 1105, 1040 - 1038, 1018 - 1016, 980
	Raman			0.44	0.02	1.3	5	0.45	0.02	1.3	0.42	0.02	1.3	/
	HSI			0.24	0.03	1.1	6	0.14	0.03	1.1	0.15	0.03	1.1	/
d4:3	NIR	239 - 777	130	0.47	95	1.4	6	0.21	130	1.0	0.32	106	1.2	/

			MIR	0.85	50	2.6	8	0.81	60	2.2	0.88	45	2.9	1745, 1626 - 1620, 1539- 1510, 1151, 1099 - 1092, 1061, 1001, 922
			Raman	0.47	93	1.4	6	0.17	117	1.4	0.19	117	1.1	/
			HSI	0.59	85	1.5	9	0.22	114	1.1	0.30	107	1.2	/
			NIR	0.42	41	1.3	6	0.22	53	1.0	0.29	47	1.1	/
d3:2			MIR	0.66	31	1.7	8	0.70	30	1.8	0.81	24	2.2	1745, 1699, 1626-1620, 1151, 1099 - 1092, 1061, 1001, 975, 922
	170 - 402	53	Raman	0.43	41	1.3	6	0.14	49	1.3	0.14	50	1.1	/
			HSI	0.50	40	1.3	9	0.26	46	1.2	0.29	44	1.2	/

793 Notes: Puree spectra and reference data from four varieties ('Golden Delicious', 'Braeburn', 'Granny Smith' and 'Royal Gala') with different fruit thinning practices for Golden Delicious
794 apples (50 - 100 fruits/ tree or 150-200 fruits/ tree), stress treatments for Braeburn apples (11 days at 24 °C or 2 months at 4 °C), two processing recipes (70 °C for 15 mins with 3000
795 rpm grinding or 95 °C for 17 mins with 400 rpm grinding) and two refining conditions (refined at 0.5 mm or not refined). All results corresponded to 10-fold full-crossed validation
796 tests. R_{cv}^2 : determination coefficient of the full-crossed validation test; $RMSE_{cv}$: root mean square error of full-cross validation test; RPD: the residual predictive deviation of full-crossed
797 validation test, LVs: the optimal numbers of latent variables. PLS-R: partial least square regression; RF-R: random forest regression; SVM-R: support vector machine regression.

Table 5. Prediction of biochemical properties of apple purees using the full cross-validation PLS, SVM and RF regression based on their NIR, MIR, Raman and HSI spectra.

Parameter	Spectra	Ranges	SD	PLS-R				SVM-R			RF-R			Key frequencies
				R _{cv} ²	RMSE _{CV}	RPD	LVs	R _{cv} ²	RMSE _{CV}	RPD	R _{cv} ²	RMSE _{CV}	RPD	NIR (nm), MIR (cm ⁻¹), Raman (cm ⁻¹), HSI (nm)
DMC (g/g)	NIR	0.16 - 0.23	0.01	0.82	0.01	2.3	7	0.73	0.01	1.9	0.78	0.01	2.1	937, 946, 1139, 1180 - 1210, 1307 - 1330, 2208 - 2254
	MIR			0.85	0.01	2.7	5	0.76	0.01	1.8	0.78	0.01	1.9	1734 - 1718, 1655 - 1637, 1084, 1061, 1024 - 1016
	Raman			0.20	0.01	1.0	8	0.02	0.01	1.0	0.01	0.01	1.0	/
	HSI			0.84	0.01	2.4	7	0.70	0.01	1.6	0.79	0.01	2.1	1037-1065, 1145, 1180-1219,1305-1338, 2286, 2421
SSC (°Brix)	NIR	11.6 - 15.8	1.1	0.83	0.4	2.5	6	0.50	0.8	1.4	0.57	0.7	1.5	944 - 946, 992, 1180- 1210, 1239, 1290 - 1330
	MIR			0.88	0.4	2.9	3	0.78	0.5	2.2	0.82	0.4	2.4	1736 - 1718, 1065 - 1055, 1022 - 1016
	Raman			0.39	0.9	1.2	9	0.18	1.0	1.2	0.15	1.0	1.1	/
	HSI			0.86	0.4	2.7	8	0.66	0.7	1.5	0.76	0.6	1.9	1048-1071, 1140-1151, 1180-1219,1290-1338
TA (meq/kg)	NIR	3.5 - 11.1	2.2	0.83	0.9	2.4	7	0.43	1.7	1.3	0.72	1.2	1.8	1017, 1049, 1167, 1374, 1534 - 1607, 1835 - 1873
	MIR			0.92	0.6	3.6	5	0.92	0.6	3.6	0.91	0.6	3.4	1736 - 1718, 1605 - 1601, 1042 - 1030, 1001 - 995
	Raman			0.71	1.2	1.8	9	0.58	1.6	1.8	0.58	1.4	1.6	/
	HSI			0.83	0.9	2.4	7	0.66	1.3	1.7	0.76	1.1	2.0	1054-1071, 1085-1214, 1293-1316, 2179-2207
pH	NIR	3.4 - 4.3	0.2	0.85	0.09	2.6	7	0.71	0.13	1.8	0.73	0.13	1.9	912, 1018, 1178, 1280 - 1305, 1835 - 1875
	MIR			0.93	0.06	3.9	5	0.91	0.07	3.6	0.91	0.07	3.6	1718 - 1715, 1094, 1065, 1034, 998, 968
	Raman			0.59	0.2	1.5	9	0.43	0.2	1.5	0.37	0.2	1.3	/
	HSI			0.85	0.1	2.6	7	0.66	0.1	1.7	0.73	0.1	1.9	1054-1065, 1185-1280,1282-1327, 2179-2207
malic (g/kg)	NIR	3.0 - 7.5	1.0	0.80	0.5	2.1	8	0.61	0.7	1.4	0.66	0.7	1.5	912, 1018, 1178, 1365, 1384, 1843 - 1860, 1908
	MIR			0.81	0.5	2.2	6	0.79	0.6	1.6	0.78	0.6	1.8	1730 - 1715, 1095 - 1082, 1001 - 995, 968 - 962
	Raman			0.27	0.9	1.2	9	0.15	0.9	1.2	0.13	1.0	1.1	/
	HSI			0.80	0.5	2.0	7	0.65	0.7	1.5	0.70	0.6	1.7	1134, 1185-1280, 1338-1367, 1843-1860, 2196-2246
fructose (g/kg)	NIR	18.7 - 84.4	13.6	0.73	7.2	1.9	8	0.51	9.7	1.4	0.52	9.8	1.4	/
	MIR			0.85	5.2	2.6	6	0.79	7.2	1.9	0.84	5.4	2.5	1155, 1094, 1065, 1056, 1034, 980
	Raman			0.66	8.5	1.6	7	0.25	8.5	1.6	0.39	10.5	1.3	/
	HSI			0.74	7.1	1.9	7	0.43	9.6	1.4	0.57	9.2	1.5	/
sucrose (g/kg)	NIR	11.0 - 81.9	17.8	0.53	11.9	1.5	7	0.40	12.3	1.4	0.41	10	1.3	/
	MIR			0.78	9.4	1.9	8	0.76	8.9	1.7	0.75	9.8	1.8	/
	Raman			0.47	12.7	1.4	5	0.33	15.5	1.1	0.35	14.8	1.3	/

glucose (g/kg)	HSI			0.61	11.1	1.6	7	0.15	16.3	1.1	0.27	15.1	1.2	/
	NIR			0.35	2.3	1.2	4	0.31	2.6	1.1	0.39	2.2	1.3	/
	MIR	10.0 - 22.5	2.9	0.44	2.2	1.3	7	0.43	2.2	1.3	0.49	2.0	1.4	/
	Raman			0.11	2.9	1.0	8	0.03	2.8	1.0	0.09	2.8	1.0	/
	HSI			0.41	2.2	1.3	4	0.27	2.4	1.2	0.37	2.3	1.3	/
AIS (FW)	NIR			0.34	2.3	1.2	5	0.36	2.2	1.3	0.31	2.5	1.1	/
	MIR	16.0 - 26.7	2.7	0.42	2.2	1.2	10	0.57	1.8	1.5	0.51	1.9	1.4	/
	Raman			0.10	2.9	1.0	6	0.10	2.7	1.0	0.11	2.90	0.9	/
	HSI			0.35	2.3	1.2	6	0.21	2.5	1.1	0.30	2.4	1.1	/

799 Notes: Puree spectra and reference data from four varieties ('Golden Delicious', 'Braeburn', 'Granny Smith' and 'Royal Gala') with different fruit thinning practices for Golden Delicious apples (50 - 100
800 fruits/ tree or 150-200 fruits/ tree), stress treatments for Braeburn apples (11 days at 24 °C or 2 months at 4 °C), two processing recipes (70 °C for 15 mins with 3000 rpm grinding or 95 °C for 17 mins
801 with 400 rpm grinding) and two refining conditions (refined at 0.5 mm or not refined). All results corresponded to 10-fold full-crossed validation tests. R_{cv}^2 : determination coefficient of the full-crossed
802 validation test; $RMSE_{cv}$: root mean square error of full-cross validation test; RPD: the residual predictive deviation of full-crossed validation test, LVs: the optimal numbers of latent variables. PLS-R:
803 partial least square regression; RF-R: random forest regression; SVM-R: support vector machine regression.

Table S1. Chemical, structural and rheological characteristics of studied apple purees.

Groups	Process	Refining	Viscosity		G'	G''	Yield stress	tan δ	d4:3	d3:2	SSC	DMC	pH	TA	malic acid	fructose	sucrose	glucose	AIS	
			<i>K</i>	<i>n</i>	Pa	Pa	-	-	-	(°Brix)	(g/g)	(meq/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	mg/g	
GD Th-	I	NR	15.4	0.24	1245.9	247.4	12.8	0.20	267.4	174.5	14.4	0.21	3.8	5.4	4.9	67.7	73.3	17.5	138.3	
		Ra	14.6	0.24	1158.8	222.5	12.6	0.19	264.5	172.4	14.1	0.20	3.7	5.5	4.6	67.2	66.4	17.1	117.8	
	II	NR	23.1	0.21	1601.3	341.6	20.1	0.21	397.0	230.7	14.4	0.21	3.8	4.9	4.0	60.5	55.2	17.0	141.8	
		Ra	20.1	0.21	1351.1	273.9	17.4	0.20	384.0	226.2	14.1	0.20	3.8	5.0	4.6	70.6	65.3	17.5	115.5	
GD Th+	I	NR	11.4	0.27	984.4	190.7	9.7	0.19	262.9	177.4	15.3	0.22	3.7	5.9	5.5	78.7	73.0	16.3	145.2	
		Ra	10.4	0.27	922.1	172.3	9.4	0.19	256.5	174.4	14.8	0.22	3.7	6.2	5.7	81.9	72.3	16.2	119.4	
	II	NR	20.0	0.22	1390.7	290.9	16.9	0.21	382.1	228.5	14.7	0.21	3.7	5.5	5.1	76.2	60.8	17.5	141.1	
		Ra	17.8	0.22	1200.4	241.5	15.0	0.20	371.4	223.8	14.5	0.21	3.7	5.7	5.2	71.6	63.1	17.6	118.3	
GS	I	NR	32.0	0.21	1835.5	385.9	25.4	0.21	598.5	314.2	12.3	0.19	3.4	10.7	7.2	44.1	29.7	20.5	182.5	
		Ra	22.3	0.22	1131.7	227.5	15.6	0.20	545.1	287.4	11.7	0.19	3.4	10.6	6.7	41.6	28.9	19.2	147.8	
	II	NR	44.8	0.20	1794.5	543.2	25.8	0.30	774.4	399.5	12.2	0.19	3.4	10.4	6.4	42.8	25.5	19.9	169.7	
		Ra	23.8	0.22	944.1	280.0	14.4	0.30	488.2	256.4	12.2	0.18	3.4	10.4	4.7	25.9	13.9	13.4	145.5	
GA	I	NR	7.3	0.33	720.2	137.8	7.6	0.19	383.1	226.6	12.6	0.19	4.0	3.8	4.1	60.7	72.3	13.5	128.4	
		Ra	7.1	0.32	675.6	125.6	7.4	0.19	372.6	223.0	12.4	0.19	4.1	3.9	4.2	65.8	71.6	13.6	119.7	
	II	NR	12.4	0.27	934.0	194.3	10.5	0.21	440.3	261.1	12.5	0.18	4.3	3.7	3.6	53.8	57.0	12.5	124.5	
		Ra	11.3	0.27	810.1	160.6	9.7	0.20	431.2	256.8	12.2	0.18	4.3	3.7	3.5	47.8	50.8	11.7	122.7	
BR	I	NR	11.2	0.28	1080.3	215.7	12.5	0.20	421.7	227.5	12.9	0.19	3.6	6.7	5.6	54.7	43.0	17.1	156.1	
		Ra	9.8	0.29	987.8	192.6	11.6	0.20	412.5	223.8	12.7	0.19	3.6	7.8	5.7	61.4	39.5	18.2	132.8	
	II	NR	22.6	0.23	1508.8	323.3	19.8	0.21	537.8	283.5	13.3	0.20	3.5	6.7	5.7	61.9	37.4	18.7	154.5	
		Ra	15.9	0.24	1054.8	210.1	13.7	0.20	499.8	267.8	13.1	0.19	3.5	6.9	5.7	61.8	41.2	18.4	122.7	
BM	I	NR	8.0	0.29	965.1	200.2	7.7	0.21	241.7	172.1	12.6	0.19	3.7	5.8	4.1	51.5	36.0	16.5	145.4	
		Ra	8.0	0.28	957.8	195.8	8.0	0.20	240.1	170.7	12.4	0.19	3.7	5.7	4.4	55.6	38.0	17.9	125.7	
	II	NR	13.9	0.24	1373.1	309.9	12.3	0.23	292.6	212.1	13.2	0.18	3.8	5.5	4.7	59.0	39.4	21.1	142.7	
		Ra	13.7	0.23	1288.3	278.7	12.0	0.22	286.7	199.8	12.7	0.18	3.7	5.5	4.9	69.2	39.8	20.8	117.8	
SD			8.7	0.04	321.7	92.5	5.2	0.03	129.7	53.2	1.1	0.01	0.2	2.2	1.0	13.6	17.8	2.9	18.3	
F-value and significance			Cultivar	192.0	120.5	50.9	73.3	74.9	1071.5	394.5	386.2	117.1	58.8	1285.8	215.0	43.4	154.9	218.1	30.4	2.8
			***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	***	*

Process	110.1	98.6	13.3	52.1	35.4	1609.1	218.6	303.4	0.02	0.4	47.2	52.6	16.1	21.4	54.9	1.8	1.6
	***	***	**	***	***	***	***	***	ns	ns	***	***	***	***	***	ns	ns
Refining	70.7	4.3	66.8	77.2	54.3	107.3	82.5	114.1	5.8	1.2	5.7	1.7	2.4	2.3	2.5	2.2	120.9
	***	*	***	***	***	***	***	***	ns	ns	ns	ns	ns	ns	ns	ns	***

805 Note: GD Th-: non-thinned Golden Delicious; GD Th+: thinned Golden Delicious; GS: Granny Smith; GA: Royal Gala; BR: crunchy Braeburn, stored at 4°C; BM: mealy Braeburn,
806 stored at 24 °C. G', G'': storage and loss modulus, at an angular frequency of 10 rad/s; AIS: Alcohol insoluble solids. Data expressed in Fresh weight (FW) values correspond to the
807 mean of 3 lots x 10 apples. Two processing strategies: Process I of 70 °C, 3000 rpm and Process II of 95 °C, 400 rpm. Processed purees with non-refining (NR) or refined at 0.5 mm.
808 In grey, ANOVA results of puree cultivar, process and refining conditions. ns, *, **, ***: Non-significant or significant at P < 0.05, 0.01, 0.001 respectively.