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Title: Intact orange quality prediction with two portable NIR spectrometers

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Keywords: acidity, fruit weight, firmness, juiciness, maturity index, NIR, orange, soluble solid content

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Abstract: Two commercial portable spectrometers were compared for orange quality non-destructive predictions by developing Partial Least Squares calibration models, reflectance mode spectra acquisition being used in both. One of them was a Vis/NIR spectrometer in which the radiation reflected by the fruit is collected and conducted by optic fiber to the three detectors (350-2500 nm) of the instrument. The other is an AOTF-NIR with a reflectance post dispersive optical configuration and InGaAs (1100-2300 nm) detector. Four orange varieties were included in calibrations. The parameters studied were soluble solids content, acidity, titratable acidity, maturity index, flesh firmness, juice volume, fruit weight, rind weight, juice volume to fruit weight ratio, fruit colour index and juice colour index. The results indicate a good performance of the predictive models, particularly for the direct NIR prediction of soluble solids content, and maturity index, the prediction of this last parameter being notable for its relevance and novelty. The RPD ratios for these parameters were in the range from 1.67 to 2.21 with the Labspec, which showed better predictive performance, and from 1.03 to 2.33 with the Luminar.

Cover letter

Title: Intact orange quality prediction with two portable NIR spectrometers

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Explanation of the manuscript's significance

In this work, two commercial portable spectrometers of Vis/NIR and NIR were compared for orange non-destructive quality prediction by developing Partial Least Squares calibration models. Four orange varieties were included in calibrations. The parameters studied were soluble solids content, acidity, titratable acidity, maturity index defined by the soluble solids content to titratable acidity ratio, flesh firmness, juice volume, fruit weight, rind weight, juice volume to fruit weight ratio, fruit colour index and juice colour index. The results indicate a good performance of the predictive models, particularly for the direct NIR prediction of the maturity index, soluble solids content, fruit weight and rind weight. The most noteworthy aspects of work are direct NIR predicting maturity index, what is reported as suitable methodology to avoid the difficulty of accurately NIR-predicting titratable acidity.

1 Intact orange quality prediction with two portable NIR spectrometers

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8

9 Abstract

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11 ~~destructive predictions by developing Partial Least Squares calibration models,~~
12 ~~reflectance mode spectra acquisition being used in both.~~ ~~One of them was a~~ Vis/NIR
13 ~~spectrometer in which the radiation reflected by the fruit is collected and conducted by~~
14 ~~optic fiber to the three detectors (350-2500 nm) of the instrument. The other is~~ ~~an~~
15 ~~AOTF-NIR with a reflectance post dispersive optical configuration and InGaAs (1100-~~
16 ~~2300 nm) detector.~~ ~~were compared for orange non destructive quality prediction by~~
17 ~~developing Partial Least Squares calibration models.~~ Four orange varieties were
18 included in calibrations. The parameters studied were soluble solids content, acidity,
19 titratable acidity, ~~soluble solids content to titratable acidity ratio~~ ~~maturity index~~, flesh
20 firmness, juice volume, fruit weight, rind weight, juice volume to fruit weight ratio, fruit
21 colour index and juice colour index. The results indicate a good performance of the
22 predictive models, particularly for the direct NIR prediction of ~~fruit weight, rind weight,~~
23 ~~juice volume,~~ soluble solids content, ~~acidity~~ and ~~the ratio soluble solids content to~~
24 ~~titratable acidity directly predicted~~ ~~maturity index.~~ ~~the prediction of this last parameter~~
25 ~~being notable for its relevance and novelty.~~ The RPD ratios for these parameters were in

26 | the range from 1.647 to 4.762.21 with the Labspec, which showed better predictive
27 | performance, and from 1.03 to 2.33 with the Luminar.

28 | **Key words:** acidity, fruit weight, ~~hardness~~firmness, juiciness, maturity index, NIR,
29 | oranges, soluble solid content.

30 |

31 | INTRODUCTION

32 | ~~Citrus fruit is fast becoming a stable food product in the daily diet of many people. The~~
33 | ~~genus Citrus includes several important fruits such as oranges, mandarins, limes,~~
34 | ~~lemons and grapefruits, orange and mandarins being the most consumed species. Spain~~
35 | ~~leads the world in fresh orange and mandarin exports (Ladaniya, 2008).~~

36 | Consumers purchase citrus fruits on the basis of quality; ~~it being as~~ a combination of
37 | characteristics and attributes ~~are~~ significant for acceptability.

38 | Citrus are non-climateric fruit, hence the ripening process stops once separated from the
39 | tree and, consequently, fruits can only be harvested and marketed once adequate
40 | maturity has been reached (Watkins, 2008). Moreover, the content of sugars and acids
41 | in citrus fruit is fairly stable before and after harvest, sugars-to-acid balance being the
42 | key to acceptability in these commodities. The content of sugars is generally measured
43 | by refractometry as soluble solids content (SSC), sugars representing the main part in it,
44 | and acids content is commonly measured as titratable acidity (TA). The ratio of soluble
45 | solids content to titratable acidity (SSC/TA) is widely used as maturity criterion for
46 | non-climateric fruits (Fellars, 1991), for the reasons indicated above, and particularly
47 | used as maturity index in citrus.

48 | Organic acids in citrus fruit rank in the 10% range in their contribution to the SSC. ←

49 | Total acidity prediction by Near Infrared Spectroscopy (NIR) has been considered

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50 difficult to achieve, due to the relatively low levels of organic acids in fruits ([McGlone](#)
51 [et al., 2003](#); Guthrie et al., 2005; ~~McGlone et al., 2003~~). Several authors have reported
52 various levels of success in predicting titratable acidity (TA) of [pineapple \(Shiina et al.,](#)
53 [1993\)](#), [plum \(Onda et al., 1994\)](#), [apple \(Sohn et al., 2000\)](#), [mango \(Schmilovitch et al.,](#)
54 [2000\)](#),~~intact~~ Imperial mandarin (Guthrie et al., 2005) ~~and~~, Satsuma mandarin
55 (Hernández et al., 2006), [pineapple \(Shiina et al., 1993\)](#), [plum \(Onda et al., 1994\)](#), [apple](#)
56 [\(Sohn et al., 2000\)](#) and [mango \(Schmilovitch et al., 2000\)](#).

57 Citrus fruit are anisotropic objects, showing different physical and chemical properties
58 when measured in different directions. Hence, equatorial measurement are reasonable
59 since at least in citrus, SSC are greatest in the distal apex of fruit decreasing towards the
60 proximal, the opposite happening with A and TA as reported by Peiris et al. (1999).

61

62 Colour is considered as one of the most important external factors of fruit quality
63 (Francis, 1995), since the fruit's appearance greatly influences the consumer. The
64 change of colour in citrus is a consequence of the maturation process, although it is also
65 highly dependent on the existence of cool temperatures at night, not always present
66 under tropical and subtropical growth conditions, which is the reason why a green citrus
67 fruit may or may not be physiologically mature (Olmo et al., 2000).

68 Fruit softening is often used as criterion for selecting the most suitable harvest date for
69 several commodities (Taylor et al., 1995; Lehman-Salada, 1996). The most common
70 method to determine the firmness of a fruit is destructive and measures its resistance to

71 penetration (Lehman-Salada, 1996; Ahumada and Cantwell, 1996; Mercado-Silva et al.,
72 1998). Other methods based on fruit resistance to compression do not necessarily
73 destroy the fruit, but they do require ~~it to be~~ harvested (Polderdijk et al., 1993;
74 Brovelli et al., 1998). Other methods, in addition to being non-destructive, can be used
75 directly on the tree, such as the use of the hand densitometer (García et al., 1998) or
76 those based on the transmission of acoustic waves through the fruit (Muramatsu et al.,
77 1996). In citrus fruit, the relationship between the degradation of the cellular wall and
78 the loss of firmness that accompanies fruit maturation has also been observed (Goto and
79 Araki, 1983). Other important attributes of the internal quality of fruits, along with
80 those mentioned above, are texture and rind thickness. In the same way, juiciness is
81 another important fruit attribute, which can eventually be reduced in citrus by factors
82 affecting the content of the juice sacs, such as freezing or excess of nitrogen fertilization
83 during summer and early autumn (Flint, 1991).

84 Excepting fruit colour, all of them are impossible to be known by the fruit appearance
85 by the consumer, whose decision to choose fruit of a desired quality is not supported by
86 sufficient objective information (Poole et al., 2006).

87 There is a need for techniques for a swift, non-destructive determination of fruit internal
88 quality, to ensure that all fruit meet a minimum level of acceptance. ~~A simplification~~
89 ~~of the analysis is an important reason for this objective. A further reason is that the~~
90 ~~conventional destructive methods of analysis are based upon a limited number of fruit~~
91 ~~samples, whereas non-destructive techniques makes it possible and the possibility~~ to
92 monitor practically all the fruit in real time are important reasons for this objective.
93 Conversely, improving the environmental sustainability of human activities is a current

94 | challenge ~~to that should~~ be emphasized, ~~achievement of which can contribute to the~~
95 | ~~Non-destructive analytical techniques can contribute~~, since it does not require
96 | chemical reagents or solvents and no waste is generated.

97 | The most suitable technology depends on ~~what is~~ the main quality parameter ~~required to~~
98 | be measured. Among several techniques, NIR has great potential for non-destructive
99 | determination of internal and maturity attributes (Abbot, 1999).

100 | The measurement modes most frequent for intact fruit SSC and TA prediction are
101 | reflectance, transmittance and interactance. Although it has been reported predictive
102 | outcomes slightly higher using transmittance regarding reflectance and interactance
103 | with intact mandarin (McGlone et al., 2003), good results using reflectance mode have
104 | been reported with mandarin (Guthrie et al., 2005; Hernández et al., 2006) and orange
105 | (Cayuela, 2008). Reflectance is the easiest mode to obtain measurements, since no
106 | contact with the fruit is required and light levels are relatively high (Mowat and Poole,
107 | 1997). In the transmission mode, the measurements are expected to be more influenced
108 | by fruit size, the amount of light penetrating the fruit often being very small, thus
109 | making it difficult to obtain accurate transmission measurements at grading line speeds
110 | (Kawano et al., 1993).

111 | ~~NIR technology has been used to determine the soluble solids content (SSC) non-~~
112 | ~~destructively in fruit such as apples (Iyo and Kawano, 2001; Hernández et al., 2003;~~
113 | ~~Zude et al., 2006), citrus (Tsuchikawa et al., 2003; Guthrie et al., 2005), peaches~~
114 | ~~(Slaughter, 1992; Peiris et al., 1997), cherries (Lu, 2001) and melons (Dull et al., 1989;~~
115 | ~~Dull et al., 1992; Ito et al., 2002; Guthrie et al., 2006), among others. Nicolai et al.~~
116 | ~~(2007) offered a review on non-destructive measurement of fruit and vegetable quality~~
117 | ~~by NIR.~~

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118 The NIR spectra are the result of the interaction of radiation with the sample, and their
119 physical and chemical properties are reflected in it. Fruit juiciness and fruit weight are
120 fruit physical properties. Successful results of NIR calibrations for citrus juiciness
121 prediction have been reported (Guthrie et al., 2005). The possibility of estimating fruit
122 weight by NIR has rarely been reported, the exploration of this possibility being of great
123 interest, since fruit weight could be added to other fruit quality parameters such as CSS,
124 TA or fruit firmness as different outputs from a single NIR measure. In fact, some good
125 outcomes have been found recently regarding NIR measuring nectarine fruit weight
126 (Pérez et al. 2009).~~In fact, good results have recently been found in nectarine fruit~~
127 ~~weight NIR measuring (Pérez et al. 2009).~~ Previous research (Cayuela, unpublished
128 data) also indicated that nectarine fruit weight can be predicted by NIR.

129 One of the advantages of NIR spectrometry is its portability when the parameter must
130 be measured *in situ*. A few models of portable NIR spectrometers of several brands are
131 available, but the applications to fruit monitoring are few. Furthermore, the technical
132 and constructive characteristics of NIR spectrometers are very diverse, and research into
133 their suitability for use in new applications is needed. Riquelme (2008) included in her
134 doctoral thesis a full revision of the commercial models of on-line NIR instruments and
135 the portable NIR spectrometers applicable to fruit.

136 In this work, the feasibility of non-destructive NIR prediction of quality parameters on
137 orange fruit, comparing ~~with~~ two commercially representative portable spectrometers,
138 using predictive models constructed by Partial Least Squares (PLS), has been evaluated.
139 The successful prediction of some parameters in this work analysed is reported for the
140 first time.

141 MATERIALS AND METHODS

142 Fruit

143 Sanguinelli, Valencia, Salustiana and Navelate oranges were hand picked, at random,
144 during the commercial harvest period, from a local experimental grove belonging to the
145 College of Agricultural Engineering, University of Huelva, transported to the laboratory
146 and used immediately or after storage at 4 °C for up to one week. The orange varieties
147 included in this study are taxonomically all them *Citrus sinensis* (L) Osb. The number
148 of samples from each variety contributing to the set of calibration is indicated in Table
149 1. The oranges were harvested at five different dates from January to April 2009, and
150 therefore, an ample diversity in the fruit quality parameters were assured. Before
151 testing, samples were taken out from the cooling and maintained at room temperature
152 (23-25 °C) for 18 h in order to allow for acclimatization to the experimental conditions.
153 Fruit were cleaned with a cloth moistened in sterile water, then dried at the lab
154 environment prior to measurement. Each fruit unit constituted the sample, and were
155 numbered in the fruit peduncle area.

156 Spectral acquisition

157 The spectral acquisition of every sample was performed using two portable
158 spectrophotometers with different optical and constructive features: Labspec (Analytical
159 Spectral Devices Inc., Boulder) and Luminar 5030 (Brimrose Corp., Maryland).

160 Labspec is a Visible/NIR spectrometer equipped with three detectors. The detector for
161 the visible range (350-1000 nm) is a fixed reflective holographic diode array with a

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162 sensitivity of 512 pixels. Wavelengths in the visible spectrum can carry information
163 relating to some of the quality parameters analyzed, such as fruit color and color of the
164 juice, and perhaps additional ones as the fruit size. The portability of the equipment is
165 assured by the weight of the spectrometer 8.5 kg. The wavelength range of 1000-1800
166 nm is covered by a holographic fast scanner InGaAs detector cooled at -25°C. The same
167 aforementioned device coupled with a high order blocking filter operates for the 1800-
168 2500 nm interval. The instrument is equipped with internal shutters and automatic offset
169 correction, the scanning speed being 100 ms. The acquisition of spectra was performed
170 using the high intensity contact probe accessory of the spectrometer, with light source
171 diameter 20 mm ~~(Fig. 1)~~, and standard SMA 905 fiber optic connectors. The whole
172 spectrum ~~(350-2500 nm)~~ was acquired, each spectral variable corresponding to 2 nm
173 interval. The repeatability of the instrument, expressed as standard deviation on the
174 average absorbance of 350 to 2500 nm of five measures of a white tile, is $6.00 \cdot 10^{-4}$. The
175 orange spectra acquisition was carried out using Indico Pro software (Analytical
176 Spectral Devices Inc., Boulder). The portability of the equipment is assured by the
177 weight of the spectrometer 8.5 kg.

178 Luminar 5030 is an AOTF (acousto-optic tunable filter) NIR spectrophotometer,
179 equipped with a reflectance post dispersive optical configuration and InGaAs (1100-
180 2300 nm) detector. The reference spectrum is automatically taken by the instrument,
181 just as an UV-VIS spectrophotometer dual beam; the beam is divided before leaving
182 and a small portion is sent to a second detector that makes the reference. The scanning
183 speed in Luminar 5030 is 60 ms. The spectrometer is formed by the hand-held unit,
184 shaped and used similarly to a 'gun', the diameter of the exit cone of the light source

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185 | being 8 mm (~~Fig. 1~~), and the computer unit; the spectrometer set, with a total weight of
186 | 5.26 Kg, offers a good portability, with 4h of autonomy using a set of batteries that
187 | allows *in situ* measuring on crop; this is an important advantage to note. The hand-held
188 | unit is equipped with a base for facultative use in the laboratory. The whole spectrum
189 | (~~1100-2300 nm~~) was acquired, each spectral variable corresponding to a 2 nm interval.
190 | The repeatability of the instrument, expressed as standard deviation on the average
191 | absorbance of 1100 to 2300 nm of five measures of a white tile, is 6.76 10⁻⁴. The
192 | signals were acquired with software Acquire (Brimrose Corp., Maryland).

193 | ~~Citrus fruit are anisotropic objects, showing different physical and chemical properties~~
194 | ~~when measured in different directions. Equatorial measurement was selected because, at~~
195 | ~~least in citrus, SSC are greatest in the distal apex of fruit, decreasing towards the~~
196 | ~~proximal, the opposite happening with A and TA, as reported by Peiris et al. (1999).~~

197 |
198 | The sample unit was the fruit, an averaged spectrum being obtained for each sample,
199 | resulting from a total 100 spectra corresponding to two measures of 50 spectra each, it
200 | for both spectrometers, taken at opposite equatorial locations, ~~according to the reasons~~
201 | ~~indicated above.~~

202 | **Figure 1**

203 | **Reference analysis**

204 | The quality attributes of each fruit were evaluated by analysis of their physical and
205 | chemical parameters. Additionally, parameters calculated arithmetically were assessed.

206 | Physical parameters

207 Fruit weight (FW, g) and rind weight (RW, g) were measured using electronic precision
208 balance (0.001 g). RW was determined once the fruit was peeled by separating the rind
209 from the flesh. For the measurement of intact fruit colour a spectral colour analyser
210 (colorimeter PCE-RGB 1002) was used, determining the same in triplicate for the same
211 fruit. This instrument has a RGB (red, green, blue) colour scale 0-1023. The Easy-RGB
212 software (Logicol Colour Technology Co.) was used for the conversion into the L, a and
213 b parameters of the Hunter scale. The results expressed by the colour index (FCI) were
214 obtained from the mathematical formula [1].

$$215 \quad CI = 1000a / Lb \quad [1]$$

216 | Flesh firmness (F, ~~KgN~~) was quantified using a hand penetrometer (TR FT-327 Turoni
217 | S.r.l., Forcy, Italy) with a 7 mm diameter cylindrical plunger, twice on the peeled fruit
218 | at the equatorial circumference. The fruit were halved through the equatorial plane and
219 | juice extracted with a commercial juice extractor. Juice volume (JV, mL) was measured
220 | with a test tube. Juice volume to fruit weight ratio was calculated and expressed as a
221 | percentage (JV/FW, %). Juice colour was determined with the same colorimeter and
222 | units above indicated for fruit colour and expressed as juice colour index (JCI). The
223 | measurement was performed on a juice sample of each individual orange fruit in a Petri
224 | plate, this measurement being made through the glass at the bottom of the plate. This
225 | procedure was used to avoid the risk of any introduction in the juice of the colorimeter
226 | light source. ~~The SSC was measured on each fruit juice by a hand help digital~~
227 | ~~refractometer (Atago Co, PAC 1 Brix Meter, Tokyo) and obtained from two replicates,~~
228 | ~~expressed as Brix units.~~

229

230 Chemical parameters

231 The SSC was measured on each fruit juice by a hand-help digital refractometer (Atago
232 Co, PAC-1 Brix-Meter, Tokyo) and obtained from two replicates, expressed as
233 percentage.

234 The acidity (A, pH) was measured on the juice of each individual fruit from two
235 replicates, using a digital pH-meter. The titratable acidity (TA) was analogously
236 measured from two replicates by direct titration of a 10 mL juice sample added with 10
237 mL distilled water, neutralized with NaOH 0.1 N until pH 8.2 and expressed as citric
238 acid (g/L).

239 Arithmetically calculated parameters

240 The maturity index reference (MI) ratio soluble solids content to titratable acidity was
241 arithmetically obtained from the ratio between SSC and TA reference analysis values
242 (SSC_p/TA_p) and in turn, by ~~the~~ arithmetical computation from SSC and TA obtained
243 using the NIR predictive models developed in this work for both parameters
244 (SSC_p/TA_p) was compared with the prediction outcomes from the model developed for
245 MI directly predicting-

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247 **Chemometrics and calibration procedure**

248 Partial Least Squares (~~Wold et al., 1983~~) models were obtained with Unscrambler 9.7
249 (CAMO Software AS, Norway). For the Labspec spectra, noise intervals 350-499 nm
250 and 2301-2500 nm were removed. Calibration tests were conducted for the Labspec to
251 eliminate spectral noise at the beginning and end of spectrum, using 500 to 2300 nm
252 wavelengths for this purpose. In turn, tests were carried out for the same spectrometer
253 excluding 600-750 nm, a range strongly affected by the skin pigment chlorophyll that
254 absorbs red light, whose absorbance band corresponds to 680 nm (~~McGlone et al.,~~

255 | ~~2003~~). This band is not included in the Luminar's wavelengths range. Exclusion of the
256 | initial and final areas of spectrum to eliminate noise, in the case of Luminar was also
257 | considered unnecessary. ~~Faulty reference analytical data were identified and eliminated~~
258 | ~~prior to calibration.~~

259 | Before calibrations, the reflectance data were transformed to absorbance, mean
260 | normalized, and optionally treated by multiplicative scatter correction (MSC) using
261 | Unscrambler 9.7. The influence of the pre-processing on the prediction of the
262 | calibration models was tested by different gap and smooth combinations for first and
263 | second gap-segment derivatives. Standard ~~N~~ormal ~~V~~ariate ~~t~~ransformation (SNV)
264 | was also tested. Full-cross internal validation (FCV) was used for building the models.
265 | Calibration tests were also conducted with different numbers of principal components in
266 | order to determine the number of PCs optimum and the results assessed in terms of
267 | standard error of cross validation (SECV). Exceptionally, where indicated in the tables,
268 | points clearly separated from the calibration sets in the scatter plots were identified as
269 | outliers and removed with Unscrambler 9.7 using its specific application for this
270 | purpose.

271 |
272 | *Validation procedure*

273 | ~~Two E~~external validation exercises were carried out using the corresponding models for
274 | predicting the parameters ~~on completely independent samples.~~ One validation exercise
275 | was conducted using 1/5 being reserved from the total reference analysed of the total
276 | number of samples for each parameter, ~~the set for validation being formed by~~
277 | Unscrambler's specific application, the first from every 5 samples taken with this
278 | purpose (V1). Other exercise was conducted for the set of samples 51 to 100,

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279 | corresponding to Sanguinelli (V2), which was excluded from the corresponding
280 | calibrations that were developed previously for this purpose.

281 | In assessing the soundness of the calibrations performance, the main considerations
282 | were the root mean square error of prediction (RMSEP) and the residual predictive
283 | deviation (RPD), described by Williams and Sobering (1996) as the ratio of the standard
284 | deviation of the reference data for the validation set to the SEP.

285 | Paired samples T test for dependent samples were also conducted to verify the results
286 | from RPD and RMSEP analysis. Not established as statistic specifically for assessing
287 | PLS model performance, T test was applied here exclusively referred to the data pairs
288 | included in the external validation exercise. For this purpose, data pairs of the reference
289 | value and the resulting prediction corresponding to the external validation sets were
290 | compared. The paired T test is a parametric procedure, useful for testing whether the
291 | means of two groups are different, where the samples are drawn in pairs. The T test was
292 | carried out using SPSS Statistics software (SPSS Inc., Chicago). The compliance with
293 | the null hypothesis in this test ($*P>0.05$) indicates that the measure NIR provides at
294 | least the same accuracy as the reference method.

295 | The prediction output from the calibration model for direct NIR MI measuring ~~the~~
296 | ~~SSC/TA ratio~~ was compared both with SSC_R/TA_R the reference values and with
297 | SSC_P/TA_P above described ~~above~~, also using the paired samples T test.

299 | **RESULTS**

300 | **Fruit NIR spectrum**

301 | Typical diffuse absorbance spectra for intact oranges acquired by both instruments
302 | (Labspec and Luminar 5030) are shown in Fig 21. The spectra from the two instruments

303 showed characteristics similar to those also previously described in oranges (Cayuela,
304 2008) or in Satsuma mandarin (Hernández et al., 2006) beyond differences regarding
305 the wavelengths acquired.

306 High intensity peaks are noted, related to the strong water absorbance bands present
307 from their first overtone at 1400 to 1500 nm and combination band at 1880-2100 nm
308 with an interval of relative intensities of high absorption, approximately between 1400
309 and 2200 nm. Absorbance falls around the 1500 nm and rises again from approximately
310 1850 nm where oscillation exists probably due to carbohydrates. Overall, the pattern of
311 the absorption curves is similar to that for other fruit such as peach (Peiris, 1997),
312 kiwifruit (McGlone and Kawano, 1998), mangoes (Budiastra et al., 1998), apple (Lu et
313 al., 2000) and cherries (Lu, 2001).

314 | Figure 21
315 |

316 **Population characterization**

317 The mean and standard deviation values of the populations of orange varieties used in
318 the calibrations and the external validations for the parameters analysed are shown in
319 | Table 1. The ~~ratio~~ SSC/TA-MI in the different varieties shows that Valencia oranges
320 | corresponded to a less advanced stage of maturation, Sanguinelli and Navelate being at
321 | approximately the same maturity stage and Salustiana showing, according to its
322 | SSC/TA-MI ratio, the most advanced maturity of the four varieties. As can be seen,
323 | wide ranges of variation of all the parameters analysed were included in the
324 | populations.

325 The characteristics of the sample sets used for the validation exercises, conducted using
326 obtained models for predicting each parameter in samples independent from the
327 calibrations sets, are shown in Table 2. The contribution of each variety to the

328 validation sets were 50 Sanguinelli, 10 Valencia, 9 Salustiana and 10 Navelate samples,
329 according to the proportion 1/5 regarding calibration sets.

330 Table 1

331 Table 2

332 **Calibration development**

333 The statistical coefficients of best calibration models with Labspec and Luminar 5030
334 for predicting orange quality parameters according to the treatment used for the two
335 instruments tested, are included in Tables 3 and 4 respectively.

336 The range from 600 to 750 nm could be affected by the skin pigment chlorophyll, as has
337 been previously indicated. Calibration tests were conducted with the Labspec excluding
338 this range, without any improvement when including it. This result probably reflects the
339 fact that no green areas were present in the skin of any of the orange samples used in the
340 calibrations. This test was unnecessary with the Luminar, since its spectral range does
341 not include 600-750 nm.

342 The calibration ~~coefficients~~ statistics for VI were relatively similar close with both
343 instruments for SSC, A, ~~SSC/TAMI~~, JV and JV/FW. Hence, with the Labspec the
344 RMSECV were 0.60, 0.12, 1.81, 7.39 and 0.03, whereas for the Luminar it were 0.67,
345 0.15, 2.06, 7.97 and 0.03 respectively for these parameters (Table 3 and Table 4). Some
346 differences were found between both spectrometers for FW, RW and ~~FF~~, the Labspec
347 showing RMSECV 19.89, 14.61 and 1.18, whereas for the Luminar it were 22.69, 17.07
348 and 1.27 (Table 3 and Table 4). All the cases, the lower values RMSECV from the
349 Labspec implies a better predictive performance for these parameters. Calibration for
350 FCI and JCI were attempted only with the Labspec, since it integrates Visible and NIR.

351 Generally, mean normalized data provided the best fits for most parameters analysed. In
352 some cases, shown in Tables 3 and 4, in both or either spectrometers, MSC treatment
353 alone or after mean normalization facilitated the best calibration coefficients.

354 Table 3

355 Table 4

356 Model external validation

357 The ~~statistical coefficients of the predictions carried out in~~ outcomes from the external
358 validation exercises V1 for each orange quality parameter with both spectrometers ~~are~~
359 shown in Table 3 and Table 4. The predictions ~~output~~ versus the analysed value of each
360 parameter in this external validation exercise are shown in Fig 32.

361 As can be seen from the validation plots, and according to the validation coefficients
362 RMSEP and RPD shown in Table 3 and Table 4, prediction accuracy was similar for
363 most fruit quality parameters with both spectrometers and slightly better with the
364 Labspec for FW, RW and ~~FF~~.

365 The validation exercise V2, corresponding to Sanguinelli, provided better performance
366 for all the parameters analyzed with the Labspec. The statistical values are shown in
367 Table 5. The best RPD with the same spectrometer in this exercise were reached for
368 SSC and MI predictions.

369 Figure 32

370 Table 5

371 DISCUSSION

372 The ~~predictive calibration for SSC showed slightly better fit with the Labspec, although~~
373 ~~it was very close to that obtained with the Luminar 5030, in which the~~ external

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374 validation exercise V1 carried out for SSC showed analogous accuracy with both
375 spectrometers, as can be deduced from the RPD ratios. ~~gave a more accurate prediction~~
376 ~~Acidity, Titratable Acidity and the SSC/TA ratio predictive calibrations were also very~~
377 ~~close between both spectrometers.~~

378 The values RMSEP in the ~~predictive models validations V1 and V2~~ for SSC 0.74 and
379 0.87 (Labspec) or 0.68 and 1.12 (Luminar) were slightly higher to those previously
380 reported by Cayuela (2008) ~~also~~ for Valencia Late orange and using reflectance (570–
381 1850 nm) with a non portable Vis-NIR spectrometer InfraXact (Foss), where RMSEP
382 0.55 is reported. In that work the direc NIR prediction of MI was not addressed.

383 For A, TA and MI the accuracy were similar in the V1 validation exercise for the
384 Labspec (Table 3) and the Luminar (Table 4). The validation V2 conducted with a
385 Sanguinelli fruit set (Table 5) showed lower RPD values for all these parameters and
386 both spectrometers, excepting for MI with the Labspec. The RPD values were higher for
387 the Labspec in this exercise, hence showing better performance.

388 ~~Both predictive calibrations for acidity (pH) and titratable acidity in this study with both~~
389 ~~spectrometers achieve lower RMSEP values than the 0.33 for titratable acidity and 0.49~~
390 ~~for pH reported previously with oranges (Cayucla, 2008), which could be attributed to~~
391 ~~the wider ranges of the values of these parameters included in the calibrations in this~~
392 ~~work.~~ For a Fantec-FQA, from the SEP and σ for pH and TA reported by Riquelme
393 (2008) can be deducted RPD values 0.68 and 0.56 using internal software for mandarins
394 and oranges, as well 0.79 and 0.37 for the same fruits using calibration developed by the
395 author, these values being lower to those reported in this work.

396 Several other results have been reported with Satsuma mandarin (Hernández et al.,
397 2006) also using reflectance and with Imperial mandarin using other optical modes

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398 (Guthrie et al., 2005; McGlone et al., 2003). However, a comparison is not
399 recommended because oranges are larger in size, ~~and with having~~ a different structure to
400 mandarin fruit. Moreover, literature about using NIR spectroscopy to SSC and pH
401 measuring in several fruit is very wide, as is referred in the introduction, thus the aim
402 here is not to demonstrate this possibility and their industrial application.

403 The RPD coefficients from the external validations for SSC, A and TA were comprised
404 in both spectrometers between ~~1.540.80~~ and 2.33. For reference, RPD ranging from
405 0.12 to 0.56 were reported using a Fantec-FOA for the same parameters (Riquelme,
406 2008). Models constructed with both spectrometers were able to determine SSC and A
407 in V1 with an accuracy approaching 95%, according to an arithmetic calculation of the
408 difference between the values estimated by NIR and reference values (data not shown).

409 The external validation V1 with the calibration for the ratio SSC/TA_{MI} showed RPD
410 very similar values in both spectrometers, this being 1.67 with the Labspec and 1.64
411 with the Luminar. The exercise V2 showed for the same coefficient RPD with the
412 Labspec 1.75, higher to the RPD 1.26 with the Luminar. Riquelme (2008) reported
413 RPD 0.25 for the same parameter and also in oranges using a Fantec-FOA., but not
414 much information scientific has been reported regarding citrus MI direct NIR
415 prediction.

416 The predictions obtained in the exercises V1 and V2 with the models for NIR
417 measuring directly ~~Soluble Solids Content to Titratable Acidity ratio (SSC/TA)_{MI}~~, were
418 compared using paired sample test T both with ~~the ratio SSC/TA arithmetically~~
419 ~~obtained from SSC and TA~~ reference analysis values ~~(SSC_R/TA_R)~~ and with the
420 arithmetical computation from SSC and TA independent NIR obtained (SSC_p/TA_p). No
421 significant differences were found in V1 between SSC/TA_{MI} predictions and

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422 ~~SSC_R/TA_Rreferences~~ (sig. 0.629) while on the contrary, there were significant
423 differences between SSC_P/TA_P and ~~SSC_R/TA_Rreferences~~ (*P = 0.039). ~~Similar result was~~
424 ~~found with V2 exercise (data not shown).~~ Therefore, ~~the ratio SSC/TA arithmetically~~
425 ~~obtained from SSC and from TA values~~MI is easy and accurately ~~if it is~~ obtained from
426 the reference analysis values ~~(SSC_R/TA_R)~~, but the arithmetical computation ~~of MI~~
427 would give worse results if these values are to be NIR obtained ~~(SSC_P/TA_P)~~, which will
428 be the case when using a NIR spectrometer in routine analysis. ~~The~~ ~~re~~fore, the ~~use of~~
429 ~~models for MI~~ direct NIR prediction is advantageous. As the SSC/TA ratio constitutes
430 the most widely used ~~maturity index~~MI, the possibility of its NIR prediction in real time
431 is of great interest, regardless of the SSC and TA values, which are also NIR measured
432 at the same moment.

433 On the other hand, ~~this~~ study ~~conducted~~ revealed that NIR prediction of ~~SSC/TAMI~~, a
434 more interesting ~~maturity index~~ than titratable acidity by itself, were more accurate than
435 TA NIR prediction, as revealed ~~in the V1 exercise~~ by the ~~statistical coefficients of the~~
436 ~~calibration and external validation exercises~~RPD for both parameters ~~SSC/TAMI~~ and
437 TA, included in Table 3 (Labspec) and Table 4 (Luminar), ~~and in the V2 exercise~~
438 ~~(Table 5) for both spectrometers~~. From these results it appears that it is a methodology
439 suitable for avoiding the difficulty of accurately NIR-predicting ~~titratable acidity~~TA, as
440 described by various authors (Mc Glone et al., 2003; Guthrie at a., 2005), since it is
441 possible to predict ~~SSC/TAMI~~ ratio directly by NIR, ~~which could be used as maturity~~
442 ~~index~~.

443
444 ~~T~~The high accuracy of the predictive calibrations for fruit weight and rind weight ~~in the~~
445 ~~V1 exercise~~ must be highlighted since, ~~for the first time~~, it makes ~~it~~ possible to measure

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446 these parameters by NIR spectroscopy in citrus. Fruit weight NIR measuring is very
447 scarcely mentioned in the literature, even for other fruit, as indicated in the introduction.
448 This accuracy is referred to each weight measurement on single fruit, it being essential
449 for the industry to ensure that all the fruit included in each bag or box has a minimum
450 suitable size or weight. The RPD from the external validation reached with the Labspec
451 for fruit weight and rind weight in the V1 exercise were 4.76 and 4.54, and with the
452 Luminar, 3.03 and 3.23, values, all cases being higher than three, the value that ideally
453 should be reached to ensure the goodness of a model (Williams and Sobering, 1996).

454
455 Regarding Juice volume calibrations models in V1 validation, they were fairly accurate,
456 coefficients being very close in both spectrometers, as shown in Tables 3 and 4. ~~The~~
457 ~~external validation for juice volume with bB~~ both spectrometers showed RPD near to
458 three in this exercise, revealing good performance. Although the volume of orange juice
459 is not generally included in trade rules for citrus fruits, the accuracy level needed has
460 not even been defined, nevertheless it is a very interesting quality parameter to be
461 monitored in each single fruit, as Riquelme (2008) reported, since citrus can eventually
462 suffer from juiciness defects.

463
464 The external validation V1 with the calibration for the ratio JV/FW with both the
465 Labspec (Table 3) and the Luminar (Table 4) ~~RPD~~ showed RPD values higher to 1.5
466 and lower to 2, what are not optimal but reveals a good predictive potential of these
467 models. ~~The statistical coefficients from the external validation exercises corresponding~~
468 ~~to each of these parameters with both spectrometers are shown in Table 3 and Table 4.~~

469

470 | Fruit flesh firmness showed ~~the value~~RPD 1.85 in the V1 external validation with the
471 | Labspec. The ability of NIR estimating orange flesh firmness with sufficient accuracy is
472 | also of great interest, since it could be used as maturity index (Olmo, 2000), although
473 | more research is needed about the relationship between orange firmness and maturity
474 | stage to establish maturity indices based upon this parameter on specific varieties. The
475 | accuracy level reached in ~~the external validation~~V1, with the Labspec for flesh firmness
476 | was 83.9%, and 79.0% with the Luminar, according to an arithmetic calculation of the
477 | difference between the values NIR estimated and reference values (data not shown).

478 | ~~This means that the difference between the model prediction and the reference analysis~~
479 | ~~were, in both cases, approximately in the order of 20%.~~

481 | The external validation V1 for FCI corresponding to the Labspec provided low and
482 | relatively good accuracy RMSEP values, with RPD 1.75. This last data indicate
483 | differences between model prediction and reference analysis of approximately 10%, on
484 | average.

485 | The statistical coefficients of the external validation V1 for predicting JCI (RPD 1.31)
486 | revealed that model performance was far from good. However, the paired T test
487 | determined no significant differences between predictions and reference values. This
488 | fact could be related with some possible inconsistent reference values that may be
489 | attributed to the methodology used for measuring juice colour and, particularly, the
490 | inclusion of the Petri plate bottom in the juice colour measurement, needing to be
491 | improved.

492 | However, considerable disagreement was found in the statistics between both validation
493 | exercises V1 and V2 conducted with both spectrometers for FW, F and JV. The RPD

494 values were clearly lower for these parameters in the exercise V2. The RPD reached for
495 the JV/FW, FCI and JCI in the V2 exercise were also lower than in V1. This facts
496 shows that the predictive potential of the technique for these parameters, when
497 measuring a set of samples not considered in the calibrations, can be lower than
498 expected.

499
500 ~~Some-Most~~ quality orange fruit parameters showed a RPD ratio lower than three, value
501 considered as threshold for an optimal validation (Williams and Sobering, 1996). ~~These~~
502 ~~parameters were soluble solids content, acidity, titratable acidity, soluble solid content~~
503 ~~to titratable acidity ratio, flesh firmness, juice volume to fruit weight ratio, and~~
504 ~~additionally, with the Labspec colour index and juice colour index.~~ However,
505 consideration of other criteria in the external validation exercises, such as paired test T
506 for all parameters studied indicated no significant differences between the laboratory
507 reference and the NIR determined values, which means that NIR was at least as accurate
508 as the reference methodologies. The unique particularity was with colour index,
509 presenting *P 0.055, which is the limit of significance, therefore reference and NIR
510 measure were very near to be different in this parameter.

511 The ~~predictions for fruit weight, rind weight and flesh firmness showed slightly~~ better
512 statistical coefficients from calibration and external validation using the Labspec. ~~This~~
513 ~~fact~~ can be due to the contact probe used in spectra acquisition with ~~theis~~
514 ~~Labspeespectrometer~~, presenting light source diameter (20 mm), larger than that of the
515 Luminar 5030 (8 mm), and, therefore, being different the area of the fruit surface
516 illuminated in both cases. This factor contributes to being able to explore a larger
517 portion of the fruit in the case of the spectrometer Labspec.

518 **CONCLUSIONS**

519 ~~The predictions of both SSC and TA and the SSC/TA relationship has been successful~~
520 ~~in the external validation by applying the corresponding calibrations developed using~~
521 ~~both spectrometers. The direct NIR prediction of SSC/TA ratio was advantageous~~
522 ~~regarding the arithmetical computation from the values of SSC and TA NIR obtained.~~
523 ~~The NIR prediction of SSC/TA was more accurate than TA NIR prediction. Therefore~~
524 ~~NIR directly predicting SSC/TA ratio can be a suitable methodology to avoid the~~
525 ~~difficulty of accurately NIR predicting titratable acidity.~~

526 ~~The predictive calibrations for Fruit Weight and Rind Weight facilitated high accuracy~~
527 ~~with both spectrometers, which is the first time that measuring these parameters by NIR~~
528 ~~spectroscopy has been reported in citrus. Also, for Juice volume and JV/FW ratio~~
529 ~~calibrations were fairly accurate.~~

531 ~~The use of NIR measurements of Fruit Colour Index together with the ratio SSC/TA~~
532 ~~and with the Flesh Firmness predictions may contribute to better defining the ripeness~~
533 ~~of citrus fruit regarding that obtained with these parameters separately.~~

534 ~~The satisfactory result obtained in the validation of models integrating four orange~~
535 ~~varieties showed that it is possible to develop predictive models for orange quality~~
536 ~~parameters in general, and not only models specific for an orange variety.~~

537
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542

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700 | (Upchurch and Throop 1994), (Kader, 1992; Polderdijk *et al.*, 1993; Blankenship *et al.*,
701 | 1997) Olmo *et al.* (2000)~~

702 |
703 |

704 | **Figure captions**

705 | ~~Figure 1. A) Labspec, contact probe. B) Luminar 5030, hand held unit~~
706 | ~~Figure 21. A) Labspec, B) Luminar 5030. Examples of absorbance spectra from the~~
707 | ~~same five oranges~~

708 | Figure 32. External validation plots V1.
709 | A) Labspec, B) Luminar 5030. RPD values at the lower right corner.

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Table 1

	Sanguinelli			Valencia			Salustiana			Navelate			Total		
	N	σ	\bar{X}	N	σ	\bar{X}	N	σ	\bar{X}	N	σ	\bar{X}	N	σ	\bar{X}
SSC	250	0.84	8.53	50	1.04	8.16	44	0.84	10.94	52	0.72	11.86	396	1.56	9.19
A	250	0.15	3.14	50	0.13	3.17	44	0.12	3.87	52	0.13	3.52	396	0.28	3.28
TA	250	0.19	0.78	50	0.21	1.48	44	0.09	0.70	52	0.16	1.06	396	3.12	9.38
MI	250	2.45	11.35	50	0.63	5.56	44	2.30	15.85	52	1.79	11.44	396	3.36	11.14
F	250	1.96	5.79	50	1.39	7.67	44	1.06	5.76	52	1.43	7.44	396	1.91	6.24
JV	250	7.25	31.88	50	9.40	48.58	44	6.29	76.80	52	7.87	74.27	396	19.80	44.55
FW	250	20.71	81.52	50	23.98	124.05	44	9.41	214.60	52	19.22	290.19	396	77.88	129.08
JV/FW	250	0.04	0.39	50	0.02	0.39	44	0.02	0.36	52	0.03	0.26	396	0.06	0.37
RW	250	14.16	43.62	50	14.70	72.09	44	6.62	128.15	52	17.59	209.72	396	59.29	78.42
FCI	250	8.62	21.05	50	8.40	15.07	44	6.08	26.48	52	3.54	18.51	396	8.35	20.56
JCI	250	88.35	62.97	50	24.52	-71.05	44	14.80	-35.62	52	30.18	-72.46	396	93.90	17.31

Table 1. Statistical data of the sets of samples and orange varieties.

SSC, soluble solids content (%); A, Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; F, flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); RW, rind weight (g); FCI, fruit colour index; JCI, juice colour index; σ , standard deviation; \bar{X} , mean.

Table 2

Parameter	Samples	Range	σ	\bar{X}
SSC	76	5.5-12.4	1.59	9.08
A	76	1.1-3.9	0.28	3.27
TA	75	0.6-2.6	0.29	0.91
MI	75	4.0-16.7	3.22	10.85
F	76	1.5-11.7	1.93	5.96
JV	74	18.0-88.0	20.58	45.00
FW	75	47.4-311.4	79.19	127.08
JV/FW	76	0.2-0.5	0.06	0.37
RW	76	18.5-228.5	60.0	76.5
FCI	72	8.7-31.0	4.64	20.54
JCI	76	-141.9-223.4	87.40	16.40

Table 2. Statistical data of the sets of samples used in V1.

SSC, soluble solids content (%); A, Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; F, flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); RW, rind weight (g); FCI, fruit colour index; JCI, juice colour index; σ , standard Deviation; \bar{X} , mean.

Table 3

Parameter	Treatment	Calibration					Validation		
		PCs	Outl.	RMSECV	R	R _{CV}	RMSEP	RPD	T
SSC	MN	10	0	0.60	0.92	0.91	0.74	2.13	0.719
A	MN, MSC	10	4	0.12	0.90	0.88	0.15	1.85	0.714
TA	MN	10	0	0.16	0.86	0.83	0.17	1.69	0.978
MI	MN	8	0	1.81	0.85	0.81	1.92	1.67	0.765
FW	MN, MSC	10	2	19.89	0.97	0.96	16.52	4.76	0.716
F	MN	7	3	1.18	0.76	0.72	1.05	1.85	0.356
JV	MN	9	3	7.39	0.92	0.91	7.05	2.94	0.511
JV/FW	MN, MSC	9	3	0.03	0.89	0.87	0.04	1.61	0.327
RW	MN	10	2	14.61	0.97	0.96	12.98	4.54	0.349
FCI	MN, MSC	8	0	3.45	0.90	0.87	2.65	1.75	0.055
JCI	MN, MSC	10	0	1.59	0.86	0.83	66.78	1.31	0.286

Table 3. Labspec. Statistics of calibrations and validations. Wavelength 500-2300 nm.

SSC, soluble solids content (%); Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; Flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); Rind weight (g); MN, mean normalisation; MSC, multiplicative scatter correction; Outl., outliers; RMSEC, root mean square error of calibration; R, coefficient of calibration; R_{CV}, coefficient of cross validation; RMSEP, root mean square error of prediction; RPD, residual predictive deviation; T, **p* value from paired samples test.

Parameter	Treatment	Calibration					Validation			
		PCs	Outl.	RMSECV	R	R _{CV}	RMSEP	RPD	T	
SSC	MN, MSC	10	0	0.67	0.91	0.89	0.68	2.33	0.273	
A	MN, MSC	10	1	0.15	0.84	0.81	0.16	1.75	0.931	
TA	MN	10	2	0.18	0.80	0.77	0.19	1.54	0.321	
MI	MN, MSC	9	1	2.06	0.79	0.74	1.96	1.64	0.313	
FW	none	9	3	22.69	0.96	0.95	26.26	3.03	0.414	
F	MSC	10	0	1.27	0.71	0.66	1.39	1.39	0.280	
JV	MN, MSC	9	2	7.97	0.91	0.91	8.00	2.56	0.977	
JV/FW	MSC	9	1	0.03	0.83	0.80	0.04	1.67	0.148	
RW	none	9	2	17.07	0.96	0.95	18.86	3.23	0.249	

Table 4. Luminar 5030. Statistics of calibrations and validations. Wavelengths 1100-2300 nm.

SSC, soluble solids content (%); Acidity (pH); TA, titratable acidity (g/L citric acid); MI, maturity index; F, flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g); RW, Rind weight (g). MN, mean normalisation. MSC, multiplicative scatter correction; Outl., outliers; RMSEC, root mean square error of calibration; R, coefficient of calibration; R_{CV}, coefficient of cross validation; RMSEP, root mean square error of prediction; RPD, residual predictive deviation; T, **p* value from paired samples test.

Table 5

Parameter	Labspec		Luminar 5030	
	RMSEP	RPD	RMSEP	RPD
SSC	0.87	2.21	1.12	1.03
A	0.13	1.05	0.40	0.80
TA	2.47	1.26	2.07	1.07
MI	1.54	1.75	2.57	1.26
FW	43.51	1.11	32.63	0.75
F	1.82	1.20	1.53	1.03
JV	8.38	1.10	12.13	0.84
JV/FW	0.04	1.18	0.05	1.10
RW	16.07	1.11	14.71	0.73
FCI	6.48	1.64		
JCI	55.69	0.67		

Table 5. Validation V2. N = 50. Wavelength 500-2300 nm.

SSC, soluble solids content (%); A, Acidity (pH); TA, titratable acidity (g/L citric acid);

MI, maturity index; Flesh firmness (N); JV, juice volume (mL); FW, fruit weight (g);

Rind weight (g); RMSEP, root mean square error of prediction; RPD, residual predictive

deviation; N, number of samples of the validation set.

Figure 1
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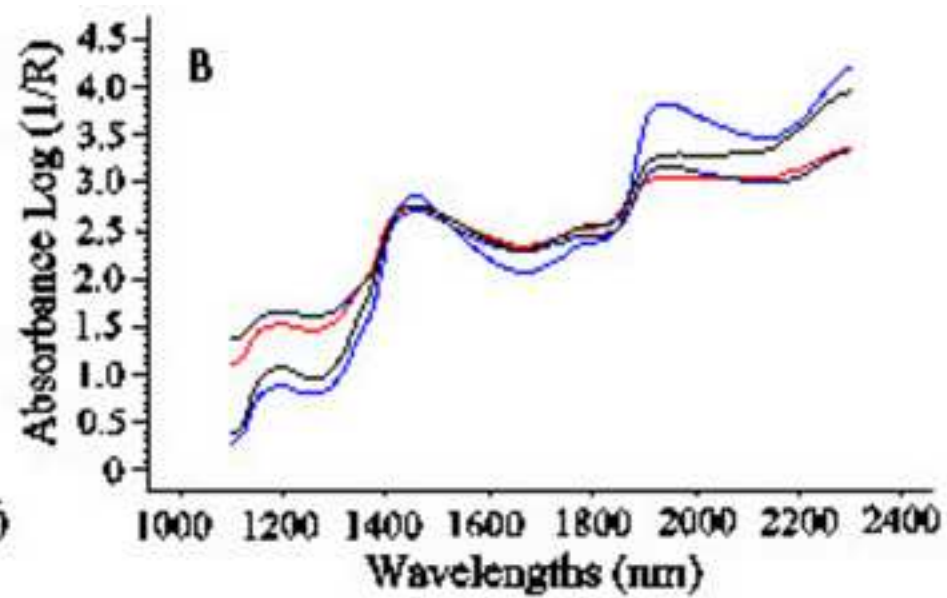
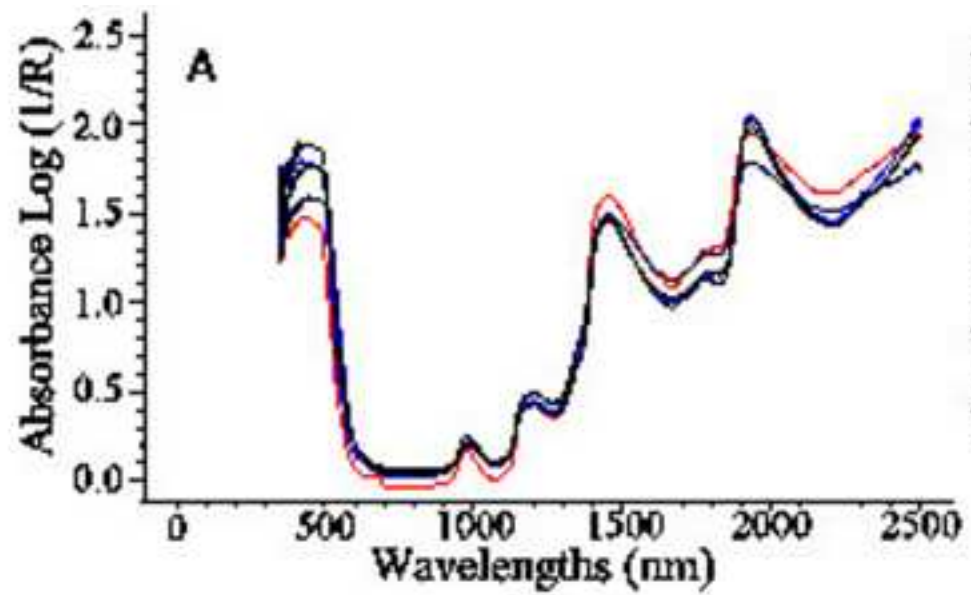


Figure 2

