



HAL
open science

Calibration transfer of intact olive NIR spectra between a pre-dispersive instrument and a portable spectrometer

L. Salguero Chaparro, B. Palagos, F. Peña Rodriguez, J.M. Roger

► To cite this version:

L. Salguero Chaparro, B. Palagos, F. Peña Rodriguez, J.M. Roger. Calibration transfer of intact olive NIR spectra between a pre-dispersive instrument and a portable spectrometer. *Computers and Electronics in Agriculture*, 2013, 96, p. 202 - p. 208. 10.1016/j.compag.2013.05.007 . hal-00864930

HAL Id: hal-00864930

<https://hal.science/hal-00864930>

Submitted on 23 Sep 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Calibration transfer of intact olive NIRS spectra between a pre-**
2 **dispersive instrument and a portable spectrometer**

3
4 **Salguero-Chaparro, L. ^{*,a}, Palagos, B. ^b, Peña-Rodríguez, F. ^a & Roger, J.M. ^b**

5 ^aIFAPA “Alameda del Obispo”, Avd. Menéndez Pidal s/n, 14004, Córdoba, Spain

6 ^bIrstea, UMR ITAP, Information-technologies-analyse environnementale-procédés agricoles, 361 rue J.F.
7 Breton, BP 5095 F-34033 Montpellier Cedex 1, France

8

9

10

11

12

13 *Corresponding author: salg_lou@hotmail.com

14 (+ 34) 957 01 61 41; Fax (+34) 957 01 60 43

15

16

17

18

19

20

21

22

23

24

25

26

27 **Abstract**

28 The recent development of new portable devices enables the use of near infrared
29 spectroscopy (NIRS) technologies in on-line industrial applications. However, the
30 numerous existing NIRS databases have been constructed with off-line laboratory
31 instruments which required a considerable effort in terms of time, labour and costs. For
32 this reason, the transfer of calibrations between devices of different characteristics is a
33 clearly crucial step. The three different standardization algorithms of Slope/Bias
34 Correction (SBC), Piecewise Direct Standardization (PDS) and Transfer by Orthogonal
35 Projection (TOP) were tested and evaluated for transferring olives quality databases
36 from an off-line NIRS monochromator (FOSS NIRSystem 6500) to a portable NIRS
37 diode-array spectrometer (CORONA 45 visNIR). The results obtained showed that the
38 use of TOP yielded the best Standard Error of Prediction (SEP) values for the fat
39 content (1.97 %) and free acidity (2.52 %) parameters, while PDS for moisture content
40 (2.24%). These results suggest that good calibration models for quality evaluation in
41 intact olives can be obtained, based on spectral databases transferred between diverse
42 NIRS spectrometers.

43

44

45 **Keywords**

46 Calibration transfer; slope/bias correction; PDS; TOP; Intact olives

47

48

49

50

51

52 **1. Introduction**

53 Near Infrared Spectroscopy (NIRS) has been successfully used by the olive oil
54 sector for the quantitative analysis of the major olive constituents such as fat content
55 and moisture in the last years (Armenta *et al.* 2010). For this reason, the implementation
56 of on-line control systems in these industries is desirable in order to determine quickly
57 and accurately the quality parameters of the olives at an initial stage of the production
58 process that could allow control the raw material (intact olives) and consequently the
59 final product (olive oil). However, the major part of applications have been developed
60 under controlled laboratory environments -i.e. off-line, a great distance away from the
61 real process in the olive mills.

62 Nowadays, by establishment of new portable devices (such as diode array
63 instruments) more robust, faster and better adapted to worse analysis conditions, the
64 direct application of this technology in the olive industry is possible. However, until
65 now, only a few studies have already been conducted for the on-line determination of
66 chemical composition in olive oil, olive pomace and olive paste (Hermoso *et al.*, 1999;
67 Jiménez-Márquez *et al.*, 2005; Gallardo-González *et al.*, 2005).

68 A key point concerning the implementation of NIR spectroscopy for olive
69 process control is to demonstrate that the large data sets obtained from off-line analysis
70 already existing, which have been developed during many years, may be used for on-
71 line industrial purposes. The construction of calibration models requires considerable
72 time, cost and effort for the collection and the measurement of the samples (Bouveresse
73 *et al.*, 1998). For that reason, an easy and rapid calibration transfer (or standardisation)
74 between instruments is necessary, in order to avoid re-measuring of the whole
75 calibration procedure.

76 In the standardization process, a calibration model developed on a *master*
77 instrument is modified in order to make it compatible with other multiple instruments
78 (*slave*) by means of a set of mathematical and statistical procedures. However, direct
79 transfer of calibration models obtained with one instrument on the same instrument after
80 a period of time, or on another different equipment will usually result in erroneous
81 predictions unless some adjustment is previously made (Andrew and Fearn, 2004). The
82 problem of calibration transfer is a significant limitation of this technique that has been
83 extensively reviewed (Wang *et al.*, 1991; De Noord, 1994; Bouveresse *et al.*, 1994;
84 Bouveresse and Massart, 1996a; Bouveresse and Massart, 1996b; Park *et al.*, 2001;
85 Fearn, 2001; Feudale *et al.*, 2002).

86 In the literature, several standardisation procedures have been developed to deal
87 with this important problem and allow the transfer of calibration models (De Noord,
88 1994; Bouveresse and Massart, 1996a; Fearn, 2001; Feudale *et al.*, 2002). There are
89 some approaches than can be used to solve the transfer problems without the need for
90 standardization (derivatives, multiplicative scatter correction (MSC), orthogonal signal
91 correction (OSC), etc.) (Feudale *et al.*, 2002). However, when the problem is not due to
92 intensity changes in the spectra if not that is related to wavelength shifts, different
93 standardization procedures can be applied. According to the strategy described in
94 Chauchard *et al.* (2004), a calibration transfer can be carried out following several
95 modes: *a priori correction* consists in correcting the spectra before applying the existing
96 calibration model; *model correction* consists in adapting the calibration model; *a*
97 *posteriori correction* consists in correcting the predictions of the existing calibration
98 model; *robust modelling* consists in building a model insensitive to the perturbation.

99 In the framework of transfer between instruments, *a priori* correction and model
100 correction are based on multivariate correction of the spectra. In the former mode, slave

101 spectra are corrected to match the master ones and inputted in the existing model. In the
102 latter mode, the spectra of the master calibration database are corrected to match the
103 slave ones and the model is recalibrated. Spectra multivariate correction may use a large
104 number of techniques, such as direct standardisation (DS) (Wang et al., 1991; Greensill
105 and Walsh, 2002; Zamora-Rojas *et al.*, 2012), piecewise direct standardisation (PDS)
106 (Bouveresse et al., 1996b; Park *et al.*, 2001; Bergman et al., 2006; Fernández-Ahumada
107 *et al.*, 2008; Igne *et al.*, 2009; Fernández-Pierna *et al.*, 2010), wavelet transform (WT)
108 (Park *et al.*, 2001; Greensill and Walsh, 2002), finite impulse response (FIR) filtering
109 without standards (Black *et al.*, 1996), boxcar signal transfer (BST) (Oliveri *et al.*,
110 2013) or the patented method proposed by Shenk and Westerhaus (1991).

111 In a posteriori correction, the existing master calibration is applied to a set of
112 slave spectra for which the responses are known. A model of the prediction error is then
113 calibrated and its inverse is applied to the future predictions. This model is generally
114 performed by a simple univariate method such as bias/slope correction (BSC) of the
115 predicted values (Osborne and Fearn, 1983; Jones *et al.*, 1993; Bouveresse *et al.*, 1998;
116 Fearn, 2001 review; Greensill and Walsh, 2002; Bergman *et al.*, 2006).

117 Robust modelling consists in building the calibration in a subspace which is not
118 affected by the influences which cause the problem of robustness. An efficient method
119 for finding this subspace is to identify the influenced subspace and to remove it by
120 means of an orthogonal projection. Depending on the way the detrimental subspace is
121 identified, several methods have been proposed, as independent interference reduction
122 (IIR) (Hansen, 2001), external parameter orthogonalization (EPO) (Roger *et al.*, 2003),
123 transfer by orthogonal projection (TOP) (Andrew and Fearn, 2004), dynamic orthogonal
124 projection (DOP) (Zeaiter *et al.*, 2006) and error removal by orthogonal subtraction
125 (EROS) (Zhu *et al.*, 2008).

126 The aim of this study was to transfer calibration models for predicting fat
127 content, free acidity and moisture in intact olives from a NIRS monochromator (FOSS
128 NIRSystem 6500) to a portable diode-array (CORONA 45 visNIR) instrument. In this
129 paper, three different representative methods for calibration transfer were tested and
130 evaluated: PDS, the most popular and widely used calibration transfer technique, for a
131 priori and model correction; SBC, the simplest and most classical, for a posteriori
132 correction and TOP, one of the most recently developed transfer method, for robust
133 modeling.

134

135

136 **2. Materials and Methods**

137

138 *2.1. Samples, spectral acquisition and reference measurements*

139 A set of 174 batches of intact olive (*Olea Europaea* L.) samples, each between
140 15 and 20 kg weight, were harvested over one crop season (October-March, 2010-2011)
141 from different plots in Andalusia (Spain).

142 Once in the lab, the olive samples were kept under controlled refrigeration at 5°C
143 and 90% relative humidity. Before spectroscopic measurements were acquired, the
144 samples were equilibrated at room temperature (25°C).

145 Spectra were collected from samples in reflectance mode ($\text{Log } 1/R$) using two
146 NIRS-instruments: (1) FNS-6500 SY-II scanning monochromator (FOSS NIRSystems,
147 Silver Spring, MD, USA); and (2) CORONA 45 visNIR diode-array spectrometer (Carl
148 Zeiss, Jena, Germany).

149 A pre-dispersive FNS-6500 scanning monochromator provided with a transport
150 module was used to measure all spectra in the scanning range of 400 to 2498 nm, at 2

151 nm interval (figure 1a). The instrument was equipped with a silicon detector in the
152 wavelength range of 400-1100 nm and with a lead sulphide detector for the range 1100-
153 2498 nm. A rectangular natural product cell with a window surface of 94.9 cm² was
154 used in order to carried out the analysis of the samples. Each spectrum was the average
155 of 32 scans. Three different charges of each sample were scanned as replicates and the
156 average spectrum was used for calculations. Spectra were recorded using ISIScan v.
157 1.26 software (Infrasoft International LLC, State College, PA, USA).

158 The second instrument was a post-dispersive single-beam diode array (DA)
159 spectrometer, CORONA 45 visNIR, working in the range from 380 to 1690 nm, with a
160 spectral wavelength interval of 2 nm (figure 1b). The DA device was equipped with a
161 silicon diode array (Hamamatsu S 3904) for the range 380-950 nm and an InGaAs array
162 for the range 950-1690. The NIRS instrument was mounted on a bracket over a
163 conveyor belt set and spectra were obtained during the movement of the samples
164 underneath the spectrometer. The optimisation of acquisition parameters were described
165 in detail by Salguero-Chaparro *et al.* (2012). The distance from the sample surface to
166 the sensing head was approximately 13 mm and the conveyor belt speed was fixed to
167 0.1 ms⁻¹. White and black spectral references were collected manually. With an
168 integration time of 5 s, 10 scans were averaged for each measurement. A total of thirty
169 spectra of the same sample were acquired and the mean spectrum was used for data
170 processing. All spectra were recorded using CORA software version 3.2.2. (Carl Zeiss,
171 Inc.).

172 Reference values for fat and moisture content in olive samples were determined
173 using official analysis methods. Fat content was obtained on olive oil samples extracted
174 by Soxhlet, according to the UNE 55030 procedure (AENOR, 1961), free acidity was
175 determined by acid-base titration according to Regulation EEC/2568/91 of the European

176 Union Commission (EC, 2003) and the moisture content was measured by oven drying
177 to constant weight at 105 °C (AENOR, 1973).

178

179 *2.2. Sample sets selection*

180 Before the calibration, test and standards sets from the two instruments were
181 selected, the spectra obtained from the FNS and CORONA equipments were previously
182 reduced to the same 646 data points (400-1690 nm). No wavelength interpolation was
183 needed because the wavelength intervals of the two devices matched. Then, raw spectral
184 data were corrected for baseline and scattering effect using the Savitzky-Golay
185 (SavGol) algorithm (21-point window, 3rd-order polynomial and 2nd-order derivative)
186 (Savitzky and Golay, 1964).

187 After spectral data preprocessing, the 174 samples obtained from each
188 spectrophotometer, forming the original dataset X_o (174 x 646), Y_o (174 x 3), were divided into
189 three groups: calibration (X_c , Y_c), standards (X_s , Y_s) and test (X_t , Y_t). For the
190 construction of these sets, Principal Component Analysis (PCA) was used. This
191 algorithm was applied on the centred Y_o matrix and then, the scores of the first
192 component was sorted in increasing order. Calibration, standards and test samples were
193 then drawn regularly from this ranking, in the following proportions: 61% (106
194 samples), 6% (10 samples) and 33% (58 samples), respectively.

195

196 *2.3. Development of NIRS calibration models*

197 Partial least squares regression (PLSR) with leave-one-out cross validation
198 (LOOCV) was used for model calibration on X_c and Y_c . Models having as many as 20
199 latent variables (LVs) were considered and the optimal model was determined by
200 choosing the number of LVs that gave the minimum in the standard error of cross-

201 validation (SECV). Coefficient of determination (R^2) between lab-measured and
202 predicted values was also reported for the optimal model.

203 Once the best calibration model for the prediction of fat, free acidity and
204 moisture content constructed based on one instrument were selected, it was then applied
205 on X_t , Y_t of the other instrument. Here, quantitative PLS models were carried out with
206 and without (models 1, *MI*) the prior performance of standardization procedures.

207

208 2.4. Calibration transfer techniques

209 Slope/bias correction (SBC), piecewise direct standardization (PDS) and transfer
210 by orthogonal projection (TOP) methods were evaluated to transfer calibration models
211 from one instrument to another. In this study, FNS-6500 instrument was used as the
212 *master* and the CORONA 45 visNIR as the *slave* device.

213

214 2.4.1. Slope/bias correction

215 Using the standard sets (X_s and Y_s), an SBC was carried out (models 2, *M2*). For
216 each response (fat content, free acidity and moisture), the model calibrated on the
217 master was applied on X_s and y_s (174×1) of the slave instrument, yielding prediction \hat{y}_s .
218 Slope and bias coefficients (b , b_0) were calculated by a linear regression between
219 predicted and actual values of y_s . The model was then tested on the test sets (X_t , y_t) of
220 the slave device and the y_t predicted (\hat{y}_t) was corrected (\hat{y}_{tc}) as follows (1):

221

$$222 \qquad \qquad \qquad \hat{y}_{tc} = (\hat{y}_t - b_0) / b \qquad (1)$$

223

224 2.4.2. Piecewise Direct Standardization

225 In this work, two different PDS approaches were evaluated. In the first of them,
226 called as PDS1, $X_t X_s$ spectra from the slave instrument were corrected, yielding
227 *standardized* $X_t X_s$, in order to become closer to the output from the master device
228 (models 3, *M3*). For that, a transformation matrix was constructed using X_s of both
229 equipments. A new LOOCV-PLS model was calibrated on $X_c X_s$ and $Y_c Y_s$ of the master
230 device and then, it was tested on the *standardized* $X_t X_s$ and $Y_t Y_s$ from the slave
231 instrument.

232 In the second approach, considered as PDS2, X_s spectra of the two instruments
233 were again applied to correct the $X_c X_s$ spectra from the master device. X_s spectra from
234 the slave and the *standardized* $X_c X_s$ spectra obtained were then used to build a new
235 LOOCV-PLS model. Finally, the model obtained was tested on $X_t Y_t$ from the slave
236 device (models 4, *M4*).

237 Different window sizes (WS) were tested (5, 9 and 31) and optimized in order to
238 compute the transformation matrix using the X_s samples.

239

240 *2.4.3. Transfer by orthogonal projection*

241 TOP method was also evaluated as a standardization procedure (models 5, *M5*).
242 Firstly, the difference between the same X_s samples measured on both instruments was
243 used to build a matrix of differences (D). Then, a singular value decomposition (SVD)
244 of D yielded its k main principal directions, in the matrix P; spectra from master
245 instrument were projected orthogonally to P; a LOOCV-PLS model was then built on
246 the orthogonalized spectra, using a maximum of 20 latent variables. The optimum
247 number k of loadings and l of latent variables were selected on the basis of the
248 minimum value obtained for SECV. Once selected the k and l values, the master
249 database was orthogonalized to the k first directions of D and a PLS model was

250 recalibrated on this base using l latent variables and tested on the samples of the slave
251 instrument.

252

253 *2.5. Computing and model evaluation*

254 Computation procedure was performed using the chemometric software Matlab
255 ver. 7.0 (The Mathworks Inc., Natick, MA, USA) and several routines created by the
256 authors, based on algorithms from the PLS Toolbox ver. 3.5 (EigenvectorResearch, Inc.,
257 Manson, WA, USA).

258 The performance of the prediction models was evaluated by the R^2 , bias and
259 standard error of prediction (SEP). The higher R^2 and the lower SEP, the better the
260 robustness.

261

262

263 **3. Results and discussion**

264

265 Figure 2 presents the raw spectra of 9 samples drawn randomly from the original
266 database, and measured by the CORONA (fig.2A) and the FNS (fig. 2B) spectrometers,
267 respectively. On the common part of both figures, some major bands can be observed.
268 The main one appears around 1450 nm. It is attributed to the first overtone of the O-H
269 bond stretching in Osborne *et al.* (1993), and is mainly due to water absorption. The
270 second one is very sharp, but appears only on some spectra, at 675 nm. It is classically
271 attributed to the chlorophyll (a and b), as in Solovchenko *et al.* (2010). At 1215 nm, one
272 can observe a band attributed in Osborne *et al.* (1993) to the second overtone of the C-H
273 bond stretching and is certainly due to the oleic acids of the olive oil. The last
274 significant band is located around 980 nm, and is assigned to the second overtone of the

275 O-H bond stretching in Osborne *et al.* (1993), and also due to water absorption. One can
276 also notice that the spectra recorded by both devices are impacted by a strong baseline
277 addition, which is due to the light scattering. Indeed, a large part of the photons which
278 are not collected by the sensors, and consequently considered as absorbed, are actually
279 scattered. This phenomenon, which causes a multiplicative effect on the signal, appears
280 additive after the log transform. Considering the visible part of the spectra on both
281 figures, two groups of spectra can be clearly distinguished. Some spectra present a very
282 high and relatively flat absorption. They correspond to very mature fruits, mainly black
283 and very absorbent in the whole visible range. The other ones present two main
284 absorbance bands, in the blue (450 nm) and in the far red (675 nm) which can be
285 assigned both to chlorophyll, and producing the green color of the non mature olives.

286 Comparing the two figures provides some other rough observations. The main
287 bands (1450, 675, 1215 and 980 nm) are very similar on both devices. On the contrary,
288 the vertical ordering of the spectra differs. The visible part differs between the two
289 devices. Some bands appear on the FNS spectra for the more mature fruits at 560 and
290 630 nm. They could traduce a balance between pigments related to chlorophyll and
291 anthocyanin. Contrarily, the spectra collected by the CORONA appear in the same zone
292 flatter and noisier. One can see a sharp break on both figures; between 980 and 982 nm
293 for the CORONA and between 1098 and 1100 nm for the FNS. Both are due to the
294 change of sensor inside the spectrometers and would cause a strong difference to be
295 compensated in the transfer procedure.

296 Table 1 gives a statistical summary of the chemical composition of the subsets
297 formed. The main goal was to build sets with comparable ranges for all the 3 responses.
298 As can be observed, the mean and standard deviation (SD) for fat content and moisture
299 parameters showed very similar results in all three sets of calibration, test and standards.

300 However, for acidity property, significant differences were appreciated between the
301 standards set and the calibration-test sets.

302 The calibration statistics of all the models developed are shown in table 2, which
303 presents for each parameter measured the best prediction in each situation, showing the
304 number of PLS factors or latent variables (LVs), the window-size (WS), the k value, the
305 coefficient of calibration (r^2) and prediction (R^2), the bias, the standard error of
306 calibration (SEC), of cross-validation (SECV), the standard error of prediction (SEP)
307 corrected for bias (SEPC) and the SEP.

308 As can be observed in table 2, the LOOCV-PLS equations for the prediction of
309 fat and moisture content based on spectra collected with the FNS instrument and applied
310 to the spectra collected with the CORONA device (*models 1*), without the performance
311 of any standardization procedure, gave a model with 4 LVs and a SEP=2.67 % to the fat
312 content parameter and a model with 7 LVs and a SEP=3.45 % to the moisture content.
313 However, for free acidity, it was observed that the *model 1* provided a very poor
314 predictive capacity for this parameter ($R^2 < 0.5$ and SEP value $> 11\%$). It should be
315 noted that the high SEP and bias values (1.61 % for fat content, 10.3 % for free acidity
316 and 1.75 % for moisture content) obtained in these models reveal the need for applying
317 a standardization procedure between spectrophotometers.

318 Table 2 also shows the results of the SBC, PDS and TOP methods applied in
319 order to transfer of calibrations for the three parameters.

320 The effect of slope/bias correction using 10 samples for the transfer is shown in
321 *models 2*. As expected, the values of bias for the predictions achieved for all properties
322 were considerably lower in these models than those obtained in the previous *models 1*.
323 For fat content, a bias of 0.41 % and a SEP of 2.54 % were obtained. For free acidity,
324 SEP and bias values were enormously reduced in both models, achieving a bias of -1.18

325 % and a SEP of 3.61 %. Finally, for moisture parameter a bias of 0.34 % and a SEP of
326 3.00 % were obtained.

327 For PDS1 and PDS2, the results obtained from *models 3* and *4* are shown, in the
328 same way, in table 2. As mentioned above (section 2.4.2), the window size (WS) was
329 optimized in order to compute the transformation matrix using the standards samples.
330 For the calibration transfer using PDS1, the lowest SEP values in *models 3* for fat
331 content, free acidity and moisture were found when a WS of 31, 9 and 5 wavelengths
332 were chosen, respectively. Concerning the results obtained in PDS2 (*models 4*), similar
333 values were obtained. For fat content, the lowest SEP value was obtained with a WS of
334 31 and it was slightly higher (2.78 %) than the ones obtained in PDS1 (SEP=2.31 %).
335 For acidity parameter, although a higher R^2 value was obtained in *model 4*, the lowest
336 SEP value was achieved in *model 3* (SEP=2.92 %). Finally, in moisture case, the SEP
337 value in *model 4* result in 2.36 % using a WS of 31 wavelengths.

338 Both PDS transfer methods have been applied using the standards set (10
339 samples) and applied to the test set (58 samples). Figure 3 shows the mean square error
340 (reconstruction error) before and after the PDS processing for the test set using a WS of
341 5. The discontinuous line corresponds to the reconstruction error between the spectra
342 measured with both devices before standardization, whereas the other line shows the
343 result after the standardization process. As can be observed from the figure 3, PDS
344 transfer allows reconstruction error to be reduced for the test set, indicating the correct
345 performance of the proposed methodology.

346 For TOP method (*models 5*), a low-SECV basin, with SECV level of 1.80 % fat,
347 was described by $k=3$ and $lv=8$, achieving a R^2 and a SEP value of 0.87 and 1.97 %,
348 respectively. For acidity property, the optimal SECV close to 3.00 % oleic acid, was
349 seen for $k=5$ and $lv=5$. In this case, a R^2 and SEP values of 0.66 and 2.52 %, respectively,

350 respectively, were obtained. Finally, the best moisture prediction ($R^2 = 0.92$ and SEP =
351 2.93 %) was carried out with $k=5$ using $lv=8$ in this *model 5*.

352 Figure 4 shows the spectra of two standards samples (#141 and #56), collected
353 by the two devices, before (original spectra) and after the TOP processing (to $k=1$ and
354 $k=5$). The effect was remarkable. As can be observed in figure 4, the two original
355 spectra (2nd derivative) of a same sample acquired with both spectrometers, showed
356 several differences in the visible region, specially between wavelengths of 675-775 nm
357 and between the wavelengths of 960-980 nm and 1450-1550 nm. After TOP, most were
358 corrected using a k value of 1. Only, for #56, differences observed in visible region were
359 not completely corrected with $k=1$. These differences totally disappeared when a $k=5$
360 was used.

361

362 3.1. Comparison of transfer methods

363 All three transfer methods (SBC, PDS and TOP) worked well for transferring of
364 the present NIRS calibrations for fat, free acidity and moisture content in intact olives.

365 For fat parameter, the best calibration transfer performance was found when the
366 TOP procedure was applied (*model 5*). Note that the SEP value after TOP
367 standardization was significantly lower (1.97 %) using 8 latent variables than the error
368 obtained in the original calibration (*model 1*) with LVs=4 (SEP=2.67 %). Additionally,
369 as can be observed in table 2, the R^2 values increased from 0.84 in *M1* to 0.87 in *M5*
370 and the bias values decreased from 1.61 % in *M1* to 0.26 % in *M5*.

371 In the same way, the application of TOP algorithm allowed to obtain the best
372 prediction results for the free acidity property. The SEP value obtained (table 2)
373 indicated that the prediction of acidity was greatly improved using TOP transferred

374 rather than untransferred models. The prediction performed in *M5* gave a SEP of 2.52
375 %, a bias of -0.36 % and a R^2 of 0.66, using only 5 latent variables.

376 Finally, for moisture parameter, it can be seen that although the fitting of the
377 models was slightly better using TOP algorithm, the predictive ability of the model
378 developed with the PDS1 method (*model 3*), was better. The initial SEP of 3.45 % and
379 the bias value of 1.75 % obtained in *MI* were highly reduced until reach a SEP=2.24 %
380 and a bias= -0.57 with a WS of 5 and using only 7 latent variables.

381 Figure 5 shows the test results of the three best models achieved from the FNS
382 master instrument for each one of the parameters evaluated.

383

384

385 **Conclusions**

386 Slope/bias correction (SBC), piecewise direct standardization (PDS) or transfer
387 by orthogonal projection (TOP) can be used for transferring multivariate calibrations
388 models for the prediction of fat content, free acidity and moisture on intact olives
389 between a pre- and a post- dispersive NIRS spectrophotometer.

390 From this study, it can be possible to affirm that the use of these standardization
391 procedures allows that the huge databases on intact olives built over several years with
392 an off-line instrument can be successfully transferred to new hand-held devices that
393 could be implanted at mill level.

394

395

396 **Acknowledgements**

397 This work is part of a PhD thesis which is being carried out by the first author, at
398 the Postharvest and Food Technology Area in the olive culture station IFAPA ‘Alameda

399 del Obispo' (Córdoba, Spain), with a grant from the National Institute for Agronomic
400 Research (INIA).

401 The authors gratefully acknowledge the financial support by the Project Number
402 DEX-560630-2008-16 (Application of NIRS technology for the on-line determination
403 on an olive mill of control, quality and food safety parameters), funded by the
404 Andalusian Federation of Cooperative Agrarian Companies (FAECA) and IFAPA. The
405 authors also would like to FMP/ffee "Andalucía se mueve con Europa" for research
406 support of this study.

407

408

409 **References**

410 Aenor, Asociación Española de Normalización y Certificación. Cuerpos Grasos.

411 Determinación del contenido en materia grasa total de la aceituna. Norma
412 UNE 55030, 1961, Madrid, España.

413 Aenor, Asociación Española de Normalización y Certificación. Materias Grasas.

414 Humedad y materias volátiles (Método de la estufa de aire). Norma UNE 55-020-
415 73, 1973, Madrid, España.

416 Andrew, A.; Fearn, T. Transfer by orthogonal projection: making near-infrared

417 calibrations robust to between-instrument variation. *Chemometrics Intell. Lab.*
418 *Syst.* 2004, 72,51-56.

419 Armenta, S.; Moros, J.; Garrigues, S.; De La Guardia, M. The Use of Near-Infrared

420 Spectrometry in the Olive Oil Industry. *Crit. Rev. Food Sci.* 2010, 50, 567-582.

421 Bergman, E.-L.; Brage, H.; Josefson, M.; Svensson, O.; Sparén, A. Transfer of NIR

422 calibrations for pharmaceutical formulations between different instruments. *J.*

423 *Pharm. Biomed. Anal.* 2006, 41, 89-98.

- 424 Black, T.B.; Sum, S.T.; Brown, S.D.; Montre, S.L. Transfer of Near-Infrared
425 Multivariate Calibrations without Standards. *Anal. Chem.* 1996, 68, 2987-2995.
- 426 Bouveresse, E.; Massart, D.L.; Dardenne, P. Calibration transfer across near-infrared
427 spectrometric instruments using Shenk's algorithm: effects of different
428 standardisation samples. *Anal. Chim. Acta* 1994, 297, 405-416.
- 429 Bouveresse, E.; Massart, D.L. Standardisation of near-infrared spectrometric
430 instruments: A review. *Vib. Spectrosc.* 1996a, 11, 3-15.
- 431 Bouveresse, E.; Massart, D.L. Improvement of the piecewise direct standardisation
432 procedure for the transfer of NIR spectra for multivariate calibration.
433 *Chemometrics Intell. Lab. Syst.* 1996b, 32, 201-213.
- 434 Bouveresse, E.; Casolino, C.; de la Pezuela, C. Application of standardisation methods
435 to correct the spectral differences induced by a fibre optic probe used for the near-
436 infrared analysis of pharmaceutical tablets. *J. Pharm.Biomed. Anal.* 1998, 18, 35-
437 42.
- 438 Chauchard, F. ; Roger, J.M. ; Bellon-Maurel, V. Correction of the temperature effect on
439 near infrared calibration – application to soluble solid content prediction. *J. Near*
440 *Infrared Spectrosc.* 2004, 12, 199–205.
- 441 De Noord, O.E. Tutorial. Multivariate calibration standardization. *Chemometrics Intell.*
442 *Lab. Syst.* 1994, 25, 85-97.
- 443 EC, 2003. European Commission regulation No 1989/2003 amending Regulation (ECC)
444 No 2568/91 on the characteristics of olive oil and olive-pomace oil and on the
445 relevant methods of analysis, 2003. Office for Official Publications of the
446 European Communities, Luxembourg.
- 447 Fearn, T. Standardisation and calibration transfer for near infrared instruments: a
448 review. *J. Near Infrared Spectrosc.* 2001, 9, 229-244.

- 449 Fernández-Ahumada, E.; Garrido-Varo, A.; Guerrero-Ginel, J.E.; Pérez-Marín, D.;
450 Fearn, T. Taking NIR Calibrations of Feed Compounds from the Laboratory to
451 the Process: Calibration Transfer between Predispersive and Postdispersive
452 Instruments. *J. Agric. Food Chem.* 2008, 56, 10135-10141.
- 453 Fernández-Pierna, J.; Vermeulen, Ph.; Lecler, B.; Baeten, V.; Dardenne, P. Calibration
454 transfer from dispersive instruments to handheld spectrometers. *Appl. Spectrosc.*
455 2010, 64, 644-648.
- 456 Feudale, R.N.; Woody, N.A.; Tan, H.W.; Myles, A.J.; Brown, S.D. Transfer of
457 multivariate calibration models: a review. *Chemometrics Intell. Lab. Syst.* 2002,
458 64, 181-192.
- 459 Gallardo-González, L.; Osorio-Bueno, E.; Sánchez-Casas, J. Application of near
460 infrared spectroscopy (NIRS) for the real-time determination of moisture and fat
461 contents in olive pastes and wastes of oil extraction. *Alimentación Equipos y*
462 *Tecnología*, 2005, 24, 85–89.
- 463 Greensill, C.V.; Walsh, K.B. Calibration transfer between miniature photodiode array-
464 based spectrometers in the near infrared assessment of mandarin soluble solids
465 content. *J. Near Infrared Spectrosc.* 2002, 10, 27-35.
- 466 Hansen, P.W. Pre-processing method minimizing the need for reference analyses. *J.*
467 *Chemometr.* 2001, 15, 123-131.
- 468 Hermoso, M.; Uceda, M.; García-Ortiz, A.; Jiménez, A.; Beltrán, G. Preliminary results
469 of NIR “on-line” measure of oil content and humidity in olive cakes from the two
470 phases decanter. *Acta Hortic.* 1999, 474, 717-719.
- 471 Igne, B.; Roger, J.-M.; Roussel, S.; Bellon-Maurel, V.; Hurburgh, C.R. Improving the
472 transfer of near infrared prediction models by orthogonal methods. *Chemometrics*
473 *Intell. Lab. Syst.* 2009, 99, 57-65.

- 474 Jiménez-Márquez, A.; Molina-Díaz, A.; Pascual-Reguera, M.I. Using optical NIR
475 sensor for on-line virgin olive oils characterization. *Sens. Actuat. B*, 2005, 107,
476 64-68.
- 477 Jones, J.A.; Last, I.R.; MacDonald, B.F.; Prebble, K.A. Development and transferability
478 of near-infrared methods for determination of moisture in a freeze-dried injection
479 product. *J. Pharm. Biomed. Anal.* 1993, 11, 1227-1231.
- 480 Oliveri, P.; Casolino, M.C.; Casale, M.; Medini, L.; Mare, F.; Lanteri, S. A spectral
481 transfer procedure for application of a single class-model to spectra recorded by
482 different near-infrared spectrometers for authentication of olives in brine.
483 *Analytica Chimica Acta*, 761, 46-52.
- 484 Osborne, B.G.; Fearn, T. Collaborative evaluation of universal calibrations for the
485 measurement of protein and moisture in flour by near-infrared reflectance. *J.*
486 *Food Technol.* 1983, 18, 453-460.
- 487 Osborne, B.G.; Fearn, T.; Hindle, P.H.; Hindle, P.T. *Practical Nir Spectroscopy with*
488 *Applications in Food and Beverage Analysis.* Longman Food Technology.
489 Longman Scientific & Technical, second edition, 1993.
- 490 Park, K.-S.; Ko, Y.-H.; Lee, H.; Jun, C.-H.; Chung, H.; Ku, M.-S. Near-infrared spectral
491 data transfer using independent standardization samples: a case study on the
492 trans-alkylation process. *Chemometrics Intell. Lab. Syst.* 2001, 55, 53-65.
- 493 Roger, J.-M.; Chauchard, F.; Bellon-Maurel, V. EPO-PLS external parameter
494 orthogonalisation of PLS application to temperature-independent measurement of
495 sugar content of intact fruits. *Chemometrics Intell. Lab. Syst.* 2003, 66, 191-204.
- 496 Salguero-Chaparro, L.; Baeten, V.; Abbas, O.; Peña-Rodríguez, F. On-line análisis of
497 intact olive fruits by vis-NIR spectroscopy: Optimisation of the acquisition
498 parameters. *J. Food Eng.* 2012, 112, 152-157.

- 499 Savitzky, A. Golay, M. J.E. Smoothing and differentiation of data by simplified least
500 square procedures. *Anal. Chem.* 1964, 36, 1627-1639.
- 501 Shenk, J.S.; Westerhaus, M.O. New Standardization and Calibration Procedures for
502 Nirs Analytical Systems. *Crop Sci.* 1991, 31, 1694-1696.
- 503 Solovchenko, A.E.; Chivkunova, O.B.; Gitelson, A.A.; Merzlyak, MN. Nondestructive
504 estimation pigment content, ripening, quality and damage in apple fruit with
505 spectral reflectance in the visible range. *Global Science Book, Fresh Produce 4,*
506 2010, 91-102.
- 507 Wang, Y.; Veltkamp, D.J.; Kowalski, B.R. Multivariate instrument standardization.
508 *Anal. Chem.* 1991, 63, 2750-2756.
- 509 Zamora-Rojas, E.; Pérez-Marín, D.; De Pedro-Sanz, E.; Guerrero-Ginel, J.E.; Garrido-
510 Varo, A. Handheld NIRS analysis for routine meat quality control: Database
511 transfer from at-line instruments. *Chemometrics Intell. Lab. Syst.* 2012, 114, 30-
512 35.
- 513 Zeaiter, M. ; Roger, J.-M. ; Bellon-Maurel, V. Dynamic orthogonal projection. A new
514 method to maintain the on-line robustness of multivariate calibrations.
515 Application to NIR-based monitoring of wine fermentations. *Chemometrics*
516 *Intell. Lab. Syst.* 2006, 80, 227-235.
- 517 Zhu, Y.; Fearn, T.; Samuel, D.; Dhar, A.; Hameed, O.; Bown, S.G.; Lovat, L.B. Error
518 removal by orthogonal subtraction (EROS): a customised pre-treatment for
519 spectroscopic data. *J. Chemometr.* 2008, 22, 130-134.

520