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

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Abstract

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

Keywords

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

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1. Introduction

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

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

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

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

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

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

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

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

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

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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 5ºC
143 and 90% relative humidity. Before spectroscopic measurements were acquired, the
144 samples were equilibrated at room temperature (25ºC).
145 Spectra were collected from samples in reflectance mode (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

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nm interval (figure 1a). The instrument was equipped with a silicon detector in the wavelength range of 400-1100 nm and with a lead sulphide detector for the range 1100-2498 nm. A rectangular natural product cell with a window surface of 94.9 cm^2 was used in order to carried out the analysis of the samples. Each spectrum was the average of 32 scans. Three different charges of each sample were scanned as replicates and the average spectrum was used for calculations. Spectra were recorded using ISIScan v. 1.26 software (Infrasoft International LLC, State College, PA, USA).

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

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

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

2.2. *Sample sets selection*

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

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

2.3. *Development of NIRS calibration models*

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

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

Once the best calibration model for the prediction of fat, free acidity and moisture content constructed based on one instrument were selected, it was then applied on X_t, Y_t of the other instrument. Here, quantitative PLS models were carried out with and without (models 1, *M1*) the prior performance of standardization procedures.

2.4. *Calibration transfer techniques*

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

2.4.1. Slope/bias correction

Using the standard sets (X_s and Y_s), an SBC was carried out (models 2, *M2*). For each response (fat content, free acidity and moisture), the model calibrated on the master was applied on X_s and $y_{s\ (174\ x\ 1)}$ of the slave instrument, yielding prediction $\hat{y}_s$. Slope and bias coefficients (b, b0) were calculated by a linear regression between predicted and actual values of y_s. The model was then tested on the test sets (X_t, y_t) of the slave device and the y_t predicted ($\hat{y}_t$) was corrected ($\hat{y}_{tc}$) as follows (1):

$$\hat{y}_{tc} = (\hat{y}_t - b0) / b \qquad (1)$$

2.4.2. Piecewise Direct Standardization

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In this work, two different PDS approaches were evaluated. In the first of them, called as PDS1, X_tX_s spectra from the slave instrument were corrected, yielding *standardized* X_tX_s, in order to become closer to the output from the master device (models *3, M3*). For that, a transformation matrix was constructed using X_s of both equipments. A new LOOCV-PLS model was calibrated on X_cX_s and Y_cY_s of the master device and then, it was tested on the *standardized* X_tX_s and Y_tY_s from the slave instrument.

In the second approach, considered as PDS2, X_s spectra of the two instruments were again applied to correct the X_cX_s spectra from the master device. X_s spectra from the slave and the s*tandardized* X_cX_s spectra obtained were then used to build a new LOOCV-PLS model. Finally, the model obtained was tested on X_tY_t from the slave device (models *4, M4*).

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

2.4.3. Transfer by orthogonal projection

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

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

2.5. Computing and model evaluation

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

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

3. Results and discussion

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

3.1. Comparison of transfer methods

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

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

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

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

Finally, for moisture parameter, it can be seen that although the fitting of the models was slightly better using TOP algorithm, the predictive ability of the model developed with the PDS1 method (*model 3*), was better. The initial SEP of 3.45 % and the bias value of 1.75 % obtained in *M1* were highly reduced until reach a SEP=2.24 % and a bias= -0.57 with a WS of 5 and using only 7 latent variables.

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

Conclusions

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

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

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