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Calibration Transfer Between NIR Diode Array and FT-NIR Spectrophotometers

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Abstract

In this paper, the piecewise direct standardization method (PDS) has been used to transfer near-infrared calibration models for the soluble solids content of apple developed for one spectrophotometer to another. The spectra were collected on three different devices: a Fourier transform (FT) spectrophotometer and two Diode Array (DA) spectrophotometers. The standardization procedure was performed on a first set with 520 Jonagored apples and a second with 1052 Jonagored and Golden apples. The performance of the standardization procedure was evaluated based on their RMSEP values. For both sets the RMSEP after carrying out the PDS procedure decreased, indicating an improvement in the prediction of SSC of apples, when spectra were collected on a DA spectrometer (*slave*) and the calibration constructed based on spectra of the same fruit but collected on a FT spectrometer (*master*).

INTRODUCTION

Using multivariate techniques, accurate near-infrared (NIR) calibration models for the prediction of a wide variety of constituents in fruit have been obtained. Nevertheless, the inability of a calibration model to be directly transferred between instruments is a significant limitation of this technique. As other authors have pointed out before (Bouveresse and Massart, 1996a; Fearn, 2001; Feudale et al., 2002), there are three main causes which introduce variation in newly recorded spectra that have not been considered in the calibration of the equipment: (i) changes in physical and/or chemical compounds of the samples, (ii) changes in the instrumental response function (different instrument, ageing of sources, replacement of some parts, etc.), (iii) changes in the environment of the instrument over time (temperature, humidity).

In order to avoid repetition of the whole calibration procedure, which is normally expensive and time consuming, different calibration transfer techniques (also known as instrumental standardization) have been developed over the past years. The term *Standardization* indicates the set of mathematical and statistical methods used to transfer the calibration model developed on a *master* instrument to another (*slave*) instrument.

Much research work has been carried out on calibration transfer of NIR spectra between NIR-spectrophotometers using different standardization approaches. Among them, univariate methods such as simple slope and bias correction (Osborne and Fearn, 1983; Wang et al., 1991) and the patented method (Shenk and Westerhaus, 1991ab);

multivariate procedures like direct standardization (DS) (Wang et al., 1991; Greensill et al., 2001; Lima and Borges, 2002) and piecewise direct standardization (PDS) (Wang et al., 1992; Bouveresse et al., 1996; Sales and Callao, 1997; Lin et al., 1997), wavelet transform (WT) (Park et al., 2001; Greensill and Walsh, 2002), as well as finite impulse response (FIR) filtering without standards (Blank et al., 1996). Moreover, new techniques have been developed by modifying various aspects of the algorithms named above (Osborne et al., 1999; Barring et al., 2001; Siska and Hurburgh, 2001; Tan and Brown, 2001; Lima and Borges, 2002; Yoon et al., 2002; Tan et al., 2002; Zhang and Small, 2003).

PDS is considered as a direct transfer technique with a good performance and has been successfully applied on a wide range of samples: spectra of corn samples (Wang and Kowalski, 1993), synthetic gasoline (Bouveresse and Massart, 1996b), fluff samples of polymers (Gilason et al., 2001), liquid organic samples (Wehlburg et al., 2002). This standardization method is based on the hypothesis that the spectral information given at a certain wavelength on the master instrument, is contained in a small spectral region of a few neighbouring wavelengths on the slave instrument. Moreover, the local multivariate models involved in PDS, which are computed per spectral window around a given wavelength of the original instrument, reduce the risk of overfitting. PDS transfers NIR spectra from the instrument on which they were collected (referred to as 'slave' instrument) to the instrument on which the calibration model is developed (referred to as 'master' instrument).

This procedure, which was developed specially to correct problems in transfer caused by shifts in peak wavelengths and by peak broadening (Wang et al., 1991), was further improved with an additive background correction by Wang and co-workers (1995). Once improved, PDS simultaneously eliminates systematic biases between the master and slave spectra (additive background) and compensates for the spectral differences between these instruments.

The feasibility of using the PDS technique for calibration transfer between photodiode array-based spectrophotometers has already been published. (Greensill et al., 1997; Greensill and Walsh, 2002). However, to our knowledge, calibration transfer between a diode array and a Fourier Transform near-infrared spectrometer in reflectance mode has not yet been reported.

The objectives of this paper are twofold: (1) to implement the calibration transfer between two Diode Array spectrophotometers (DA) based on a PDS procedure; (2) to study the feasibility of PDS to transfer a Partial Least Square (PLS) calibration model developed on a Fourier Transform NIR (FT-NIR) spectrophotometer to a DA spectrophotometer, for the prediction of the soluble solids content (SSC) in apples.

MATERIALS AND METHODS

Samples and measurements

The experiment was performed with apples from two different cultivars, Jonagored and Golden, which were harvested weekly from July 2004 until the commercial harvest date, in three different Belgium orchards (Velm, Rillaar and Linter). Two data sets were used. The first set (set₁) consisted of 520 spectra of *Jonagored* apples and the second set (set₂) contained 1052 spectra (526 *Jongored* and 526 *Golden*).

All the samples were equilibrated at room temperature before the spectra were acquired. For each apple a reflectance spectrum was obtained on two equatorial positions

(red and green side). Three different spectrophotometers were used: a Fourier transform spectrophotometer (FT) (InfraProver, Bran&Luebbe, Norderstedt, Germany) and two Diode Array (DA) spectrophotometers (Corona for Agriculture and Food (Cora), Carl Zeiss AG, Germany). Abbreviations are mentioned in Table 1. The DA_V spectrophotometer was located in the VCBT laboratory (Flanders Centre of Postharvest Technology) while the DA_H spectrophotometer was in the laboratory of an experimental station (National Experimental Station for Chicory, Herent, Belgium).

Each reflectance spectrum was divided by a white reference spectrum recorded on a BaSO₄ disc for the DA spectrophotometers, and a Teflon plate for the FT. Additionally, each measured reflection spectrum was the average of 10 individual optical scans with 2nm increments for the DA devices and 24cm⁻¹ increments for the FT. For further calculations the average spectrum of the two sides, as well as the common wavelength range between both devices, from 1020 to 1690 nm, was used. The FT spectrophotometer was considered as *master* instrument while the DA spectrophotometers were considered as *slaves* spectrophotometers. The main reason for this selection was that a robust PLS calibration model to predict SSC with FT-NIR spectra was developed in the past.

The reference measurements were obtained by determining the soluble solids content (SSC) from a drop of apple juice, using a digital refractometer (PR-101, Palette Serie, Atago Co. Ltd., Tokyo, Japan). The measurements were taken at the same position where the spectra were acquired and averaged.

Data analysis

Since both devices used a different representation for the spectra (wavelength versus wavenumber), FT spectra were interpolated to fit the DA spectra, by piecewise cubic Hermite interpolation in MATLAB (The Mathworks, Inc., Natick, MA, USA). Multiplicative Scatter Correction (MSC) pre-treatment was also applied to all data. This pre-treatment, as well as the SSC calibration models on the *master* and *slave* devices, were developed by the statistical program for multivariate calibration The Unscrambler (CAMO AS, Trondheim, Norway). Calibrations against SSC were built with the entire data from each set and the calibration coefficients were determined by Partial Least Squares prediction (PLS1) with cross-validation (n° of segments=20 and samples per segment=52). SSC prediction performance was expressed for the *master* instrument in terms of the root mean squared error of prediction (RMSEP).

To transfer the SSC calibration model between FT and DA instruments, the DA spectra were transformed by PDS as if they were measured on the FT spectrophotometer. To transfer the calibration model between the two DA instruments the same PDS procedure was applied. The standardization and calibration transfer programs were written in MATLAB (the PLS_Toolbox, Eigenvector Research, Inc., Manson, WA, USA). The evaluation of PDS performance was done by comparing the RMSEP of the SSC model derived on the *master* and RMSEP of the standardized *slave* spectra using the original FT-model for SSC. The RMSEP was calculated as:

$$RMSEP = \sqrt{\frac{\sum_{i=1}^I \left(\hat{y}_i - y_i \right)^2}{I}}$$

where \hat{y}_i is the predicted SSC value, y_i is the actual SSC value, and I is the number of samples.

RESULTS AND DISCUSSION

In a preliminary experiment (data not shown) the number of samples to be included in the standardization subset was optimised and selected in order to compute the transformation matrix. For set₁, a subset₁ of 30 Jonagored apples was selected, while for set₂, a subset₂ with a total of 30 apples (Jonagored and Golden) was used. The number of principal components (PC's) and window size (WS) were determined for each local model (PC's=3 and WS=51) in the PDS procedure.

The standardized and original spectra, from an arbitrary chosen sample that is not included in the standardization set, are compared in Fig. 1. The difference between the FT and DA spectra after the PDS procedure has been reduced considerably for all three cases, the master spectra and the standardized spectra seem to match quite well.

The calculated RMSEP values are given in Table 2. The values of RMSEP for both set₁ and set₂, measured on the *slave* instrument before standardization reveal that the spectra measured on the slave need to be standardized before applying the calibration model. After the standardization procedure there was an improvement in the prediction of SSC as illustrated by the decrease in RMSEP. The higher differences between RMSEP and RMSEP_a for set₂ indicated that the transfer matrix obtained from set₁ leads to better standardizations than the transfer matrix calculated from set₂.

Surprisingly, a better standardization between FT and DA spectrometers was obtained than between similar spectrophotometers. However, in this case, there was a better correction of the differences between DA instrumental responses when in set₂ than in set₁.

CONCLUSIONS

The performance of the developed PDS program gave encouraging results when transforming the DA spectra as if they were measured on a FT-NIR spectrophotometer. The differences between the master reflectance spectra and the standardized slave spectra have been considerably reduced and the RMSEP values have decreased a lot in comparison with the values obtained before the standardization procedure. Unexpectedly, when using the transformed DA_H-spectra to predict the SSC based on the model derived on the DA_V, the RMSEP calculated was higher than the RMSEP obtained between DA and FT-NIR spectrometers. More analysis is required to further explore this result.

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Tables

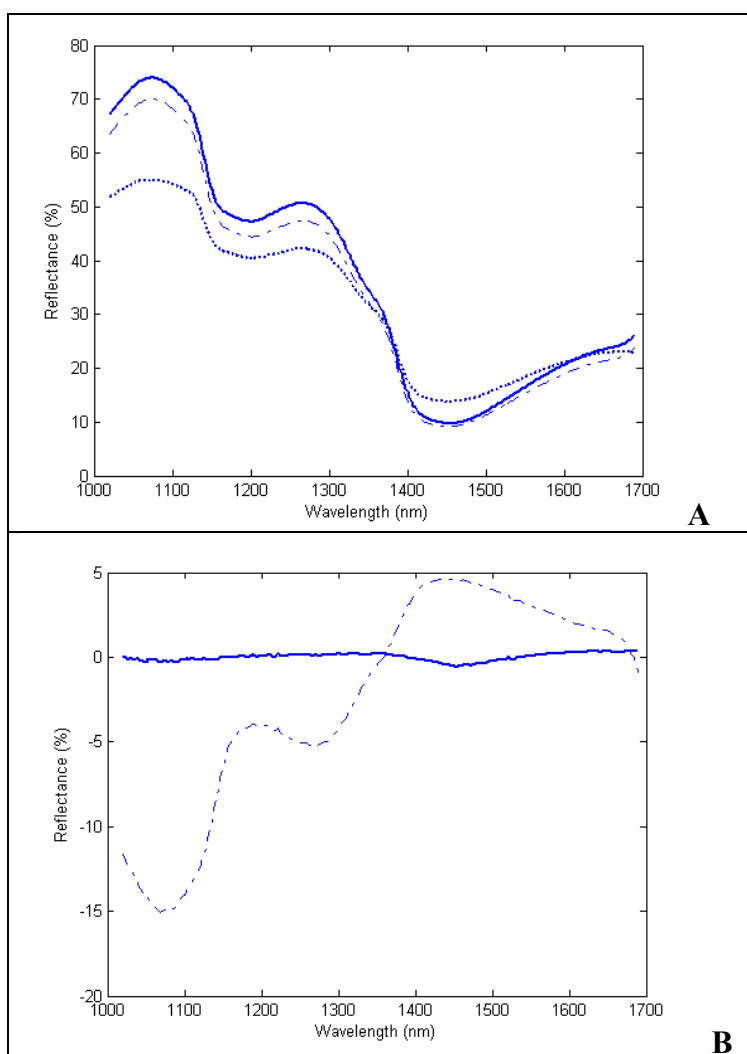
Table 1. List of abbreviations.

| Abbreviations | Explanation |
|---------------------------------------|--|
| FT | Fourier transform spectrophotometer |
| DA_H | Diode array spectrophotometer from National Experimental Station for Chicory, Herent, Belgium. |
| DA_V | Diode array spectrophotometer from VCBT laboratory |
| DA_V^{stand} | Diode array spectra (VCBT) after PDS method |
| DA_H^{stand} | Diode array spectra(Herent) after PDS method |
| RMSEP_b | Root mean squared error of prediction before the PDS |
| RMSEP_a | Root mean squared error of prediction after the PDS |

Table 2. Calibration transfer performance in terms of RMSEP for the prediction of SSC for apples, using spectra collected on a *slave* spectrometer and a calibration generated on spectra of the same fruit, collected on a *master* instrument. The RMSE for the prediction of SSC for all three master instruments is also given.

| Apple population | Set 1 | | | Set 2 | | |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Spectrophotometer | FT | DA _V | DA _H | FT | DA _V | DA _H |
| RMSEP | 0.521 | 0.466 | 0.469 | 0.51 | 0.493 | 0.466 |
| Master | FT | FT | DA _V | FT | FT | DA _V |
| Slave | DA _V | DA _H | DA _H | DA _V | DA _H | DA _H |
| RMSEP_b | 15.2468 | 32.5558 | 25.1332 | 6.4946 | 6.1975 | 33.7501 |
| RMSEP_a | 0.8838 | 0.8991 | 2.6261 | 1.0123 | 1.0204 | 1.9568 |

Figures



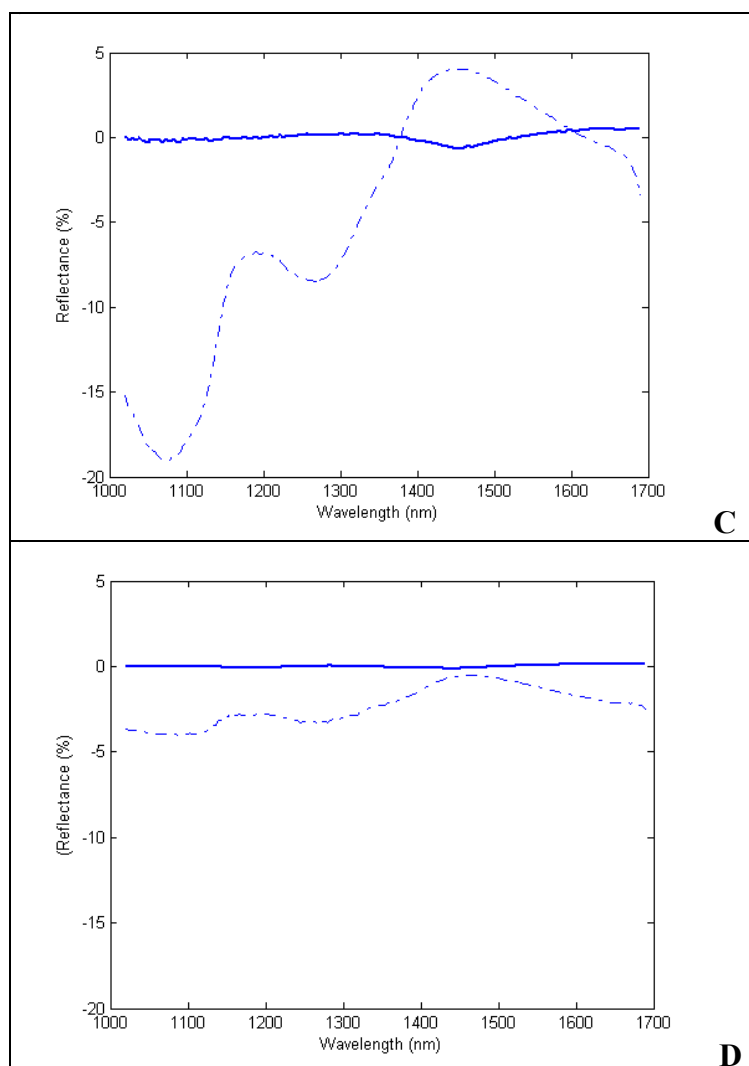


Fig. 1. **A)**: Representative spectrum of the same Jonagored apple measured by three different spectrophotometers: DA_V (solid line), DA_H (dash-dot line) and FT (dotted line), before the standardization procedure. In the images **B**, **C** and **D** we can see the differences between the spectrum of the same apple, measured on different spectrophotometers (*master* vs *slave*), before (dash-dot line) and after (solid line) the performance of PDS procedure. **B)**: The spectra were measured on FT (*master* instrument) and on DA_V (*slave* instrument). **C)**: The spectra were measured on FT (*master* instrument) and on DA_H (*slave* instrument). **D)**: The differences between the spectra taken on DA_V (*master*) and on DA_H (*slave*) are shown.

Transfert d'un modèle entre spectrophotomètres infra-rouge à transformée de Fourier et à réseau de diodes

Mots clés : *Spectroscopie infra-rouge, PDS, pomme, extrait sec soluble*

Résumé

Dans cet article, la méthode de standardisation directe par morceaux (PDS en anglais) est utilisée pour transférer un modèle de dosage de l'extrait sec soluble des pommes d'un spectromètre vers un autre. Les spectres ont été acquis sur 3 appareils : un spectromètre à transformée de Fourier (FT) et deux spectromètres à réseau de diodes (DA). La procédure est appliquée sur un premier ensemble de 520 pommes Jonagored, puis dans un deuxième temps, sur 1052 fruits, Jonagored et Golden. La performance est mesurée par le RMSEP. Dans les deux cas, après la PDS, la valeur du RMSEP baisse, indiquant une amélioration des performances pour les mêmes fruits, lorsque le modèle est construit à partir des spectres acquis sur le spectromètre FT et transféré vers le spectromètre DA.
