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Calibration transfer between NIR diode array and FT-NIR spectrophotometers for measuring the soluble solids contents of apple

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Abstract

Prediction models of soluble solids contents of fruit obtained with a specific near-infrared spectrophotometer cannot be directly transferred to another spectrophotometer. In this research, a piecewise direct standardization method has been used for this task. As a result, a calibration model for soluble solids contents of apple developed on a Fourier transform based spectrophotometer has been successfully transferred to a diode array (DA) spectrophotometer. The standardization procedure was performed on a data set of 477 Jonagored apples and root mean squared error of prediction of 0.85° Brix was obtained. Additionally, the necessity of calibration transfer procedures between two DA spectrophotometers of the same type and model has also been found.

Keywords: Apple; Quality; Soluble solids content; NIR; Spectroscopy; Calibration transfer; PDS

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1. Introduction

The potential to measure quality attributes such as sugar content and firmness of intact fruit such as nectarines and peaches, apples and kiwifruit has been evaluated extensively during the last 10 years (Slaughter, 1995; Lammertyn et al., 1998; McGlone and Kawano, 1998; Ventura et al., 1998; Schaare and Fraser, 2000; McGlone et al., 2002). In NIR spectroscopy, NIR radiation is guided into the product, and some of the backscattered radiation is captured and related to variables of interest via multivariate statistical techniques. Because of their high acquisition speed, diode array systems are more suitable than Fourier Transform instruments to be mounted on high speed grading lines in such a way that, grading based on internal quality attributes rather than external appearance comes within reach.

The inability of a calibration model developed on one instrument to be directly used on another one, even between two devices of the same type, is a significant limitation of this technique. This seriously hampers widespread application as this would mean that the calibration model has to be constructed again for every spectrophotometer. As other authors have pointed out before (Bouveresse and Massart, 1996a; Fearn, 2001; Feudale et al., 2002b) 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.) and (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* (or *primary*) instrument to another instrument (*slave* or *secondary*).

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On the other hand, some approaches are also used to solve the transfer problems that eliminate the need of standardization. Robust calibrations models that are not sensitive to instrumental responses can be made by using appropriate pre-treatment techniques (derivates, multiplicative scatter correction (MSC), orthogonal signal correction (OSC), standardized normal variates (SNV), etc.) (Feudale et al., 2002a), selecting wavelengths (Swierenga et al., 1998) or including several instruments in the calibration set (Büchmann, 2000; Tillmannn et al., 2000). Pretreatment is suitable when the problem is related to absorbance shifts, the instruments involved are very similar and the instrumental differences are small. When selecting wavelengths, only those wavelengths which are robust enough against instrumental differences (wavelength variation has no effect on the regression coefficients) will be selected and used afterwards to build the multivariate calibration models. However, this approach, which was already suggested by Mark and Workman (1988) to make calibrations robust to wavelength shifts, is not appropriate to correct intensity differences or peak broadening in spectra.

In order to solve the problem of transferability when either quite different NIR spectrophotometers or wavelength shifts are involved, different standardization approaches have been developed. Among them, univariate methods are available such as simple slope and bias correction (Osborne and Fearn, 1983) and the patented method proposed by Shenk and Westerhaus (1991a,b). This method works well when correcting wavelength shifts or linear intensity differences in spectra, but it cannot cope with peak broadening. To correct more complicated effects and peak broadening, multivariate standardization procedures such as direct standardization (DS) (Wang et al., 1991; Greensill et al., 2001; Lima and Borges, 2002), piecewise direct standardization (PDS) (Wang et al., 1992; Bouveresse et al., 1996; Sales et al., 1997; Lin et al., 1997), wavelet transform (WT) (Park et al., 2001; Greensill and Walsh, 2002) and finite impulse response (FIR) filtering without standards (Blank et al., 1996) are used. New techniques to improve the transferability have been developed by modifying various aspects of the algorithms named above (Osborne et al., 1999; Bärring et al., 2001; Siska and Hurburgh, 2001; Tan and Brown, 2001; Yoon et al., 2002; Tan et al., 2002; Zhang and Small, 2003). The PDS algorithm is fast and easy to implement, and is now available in commercial chemometrics software. Also, good results have been obtained with this algorithm (Greensill and Walsh, 2002; Bergman et al., 2006).

The feasibility of using the PDS technique for calibration transfer between photodiode array-based spectrophotometers has already been published by Greensill et al. (2001) and Greensill and Walsh (2002). However, transfer of calibration models for the soluble solids contents of fruit between a diode array and a Fourier Transform near-infrared spectrometer in reflectance mode has not yet been reported. Moreover, it must be noted that while a silicon diode array (300–1100 nm) was used by Greensill and co-workers, in our research we used an InGaAs diode array (950–1700 nm).

The objectives of this paper were, therefore, two-fold: (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 near infrared (FT-NIR) spectrophotometer to a DA spectrophotometer, for the prediction of the soluble solids contents (SSC) in apples.

2. Materials and methods

2.1. Samples and spectral acquisition

A training set and a validation set were considered in this study. In both cases, twenty 'Jonagored' apples were harvested weekly from July 2004 and 2005, respectively, until the commercial harvest date (23 September and 20 September, respectively), in three different Belgium orchards (Velm, Rillaar and Linter). The training data set consisted of 477 spectra while the validation data set consisted of 625 spectra.

All the apples were equilibrated at room temperature before the spectral measurements were acquired. 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). The spectra were acquired in the wavelength range between 380 and 2000 nm for both DA instruments, and between 9984 cm^{-1} (1001.60 nm) and 4008 cm^{-1} (2495.01 nm) for the FT-NIR spectrophotometer. One DA-instrument ($\mathrm{DA_v}$) and the FT-NIR spectrophotometer were located in the Flanders Centre of Postharvest Technology (Heverlee, Belgium) (VCBT). The measurements on the second DA-spectrophotometer ($\mathrm{DA_H}$) were carried out in the National Experimental Station for Chicory (Herent, Belgium) and were acquired within the same morning.

The DA spectrophotometers were equipped with a silicon diode array (Hamamatsu S 3904) for the range 380–950 nm and an InGaAs array for the range 950–1700 nm; the light source consisted of a 9 W, 5 V stabilised Halogen lamp. The FT-NIR spectrophotometer was equipped with a Tungsten halogen lamp and PbS detector.

Light sources and spectrophotometers were switched on two hours prior to the acquisition of the spectra. For each apple a reflectance spectrum was obtained on two equatorial positions (red and green side) and fruit were covered by a black box to avoid scattered environmental light during the measurement. The spectra acquired on the DA spectrophotometer were corrected for the dark current response of the detector. Each reflectance spectrum was divided by a white reference spectrum recorded on two different $\mathrm{BaSO_4}$ discs for the DA spectrophotometers, and a Teflon plate for the FT. Additionally, each measured spectrum was the average of 10 individual optical scans with 2 nm increments for the DA devices and 24 cm^{-1} increments for the FT. The resolution of both instruments was different. The FT spectrophotometer had a resolution of 24 cm^{-1} in wavenumbers what is equivalent to a spreading resolution on the wavelength scale of 2.4 nm at 10,000 cm^{-1}, 6.7 nm at 6000 cm^{-1} and up to 15 nm for the highest wavelengths. The dispersive system had a resolution of 6 nm for the range of 950–1700 nm. For further calculations the average spectrum of