Calibration transfer from reflectance to interactance–reflectance mode: use of mathematical pretreatments

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Introduction

Traditional applications of near infrared (NIR) spectroscopy in agriculture products are being developed in either reflectance or transmittance mode, and calibration transfer from these modes to fibre-optic analysis modes might prove a useful way of saving money and effort. Most methods for calibration transfer between different instruments involve the use of sealed reference cups but, as fibre optic analysis does not use cups, other methods of calibration transfer are required.[1]

Within the framework of the STAFANIR project,[2] highly accurate European calibrations were developed for barley, wheat and maize. These equations were successfully transferred from a master instrument to several satellite instruments of different brands and models. However, all satellite instruments tested were using reflectance analysis.

The primary purpose of this paper was to study the effect of different mathematical pretreatments of log $1/R$ data on the performance of calibration equations obtained for reflectance analysis; a secondary aim was to determine whether use of these mathematical transformations is sufficient to implement the transfer of European calibrations from reflectance to interactance–reflectance mode.

Material and methods

Samples and reference data

Three sets of ground cereals (barley, wheat and maize) were defined as calibration sets. These samples and the reference data were provided by the STAFANIR project.[2] The chemical composition of the calibration sets is shown in Table 1. The validation sets consisted of 92 ground samples of barley, 74 of maize and 76 of wheat.

Table 1. Reference data (expressed as %) of calibration sets.

Set (parameter)	N	Mean	Minimum	Maximum	SD
Barley (CP)	177	11.86	7.38	17.19	2.83
Wheat (CP)	225	12.16	8.54	17.71	2.51
Maize (Oil)	180	5.27	3.08	9.30	1.49

NIR hardware

Reflectance spectra for calibration sets were obtained on a Foss NIRSystems 6500 monochromator, from 400 to 2498 nm, every 2 nm. Analysis was performed using a spinning module and samples were scanned on standard ring cells.

Validation spectra were scanned at the same time by two scanning monochromators, in reflectance and interactance–reflectance modes. For reflectance analysis, a Foss NIRSystems 6500 without auto-gain detectors, provided with a spinning module, was used. Samples were scanned in standard ring cells. A Foss NIRSystems model 6500 scanning monochromator with auto-gain detectors was used to measure interactance-reflectance spectra from 400 to 2498 nm, at intervals of 2 nm. Analysis

Table 2. Combination of mathematical pretreatments used for calibration development.

Equation	Scatter Correction	Derivative	Equation	Scatter Correction	Derivative
1	None	None	19	DT	2,10,10,1
2	SNV	None	20	SDT	1,5,5,1
3	DT	None	21	SDT	1,10,10,1
4	SDT	None	22	SDT	2,5,5,1
5	Standard MSC	None	23	SDT	2,10,10,1
6	Weighted MSC	None	24	Standard MSC	1,5,5,1
7	Inverse MSC	None	25	Standard MSC	1,10,10,1
8	None	1,5,5,1	26	Standard MSC	2,5,5,1
9	None	1,10,10,1	27	Standard MSC	2,10,10,1
10	None	2,5,5,1	28	Weighted MSC	1,5,5,1
11	None	2,10,10,1	29	Weighted MSC	1,10,10,1
12	SNV	1,5,5,1	30	Weighted MSC	2,5,5,1
13	SNV	1,10,10,1	31	Weighted MSC	2,10,10,1
14	SNV	2,5,5,1	32	Inverse MSC	1,5,5,1
15	SNV	2,10,10,1	33	Inverse MSC	1,10,10,1
16	DT	1,5,5,1	34	Inverse MSC	2,5,5,1
17	DT	1,10,10,1	35	Inverse MSC	2,10,10,1
18	DT	2,5,5,1			

was performed using a fibre optic probe (NR-6775). Three spectra were collected and averaged for each sample at different locations, in order to reduce sampling errors.

NIR software and chemometric treatments

All spectra were manipulated and processed and all calibration equations were obtained, using ISI software NIRS3 ver. 4.0 and WINISI ver. 1.5 (Infrasoft International, Port Matilda, PA, USA).

A total of 35 different calibration equations were obtained for each cereal and chemical parameter (Table 2). All calibrations were obtained for the spectral range 1100–2200 nm, which was found to be free of spectral error for interactance–reflectance analysis in a previous study.[3] The modified partial least squares (MPLS) regression method was used for obtaining equations.[4,5] The mathematical pretreatments used were standard normal variate (SNV),[6] detrending (DT),[6] SNV and DT (SDT), the three versions of multiplicative scatter correction (MSC)[7] included in WINISI software (Normal MSC, Weighted MSC and Inverse MSC) and four different derivative math treatments. The derivative math treatments are referred to by a four-digit notation (a,b,c,d).[8]

NIR equations were evaluated by examining the statistical values obtained for 1-VR (coefficient of determination of cross-validation) and standard error of cross-validation ($SECV$). Calibration transfer was evaluated by the statistic R^2 and standard error of differences (SED) calculated for the predicted values of the validation samples scanned on the two instruments and in both analysis modes.[9]

Results and discussion

Calibration statistics (R^2 and $SECV$) for the different equations and products are shown in Figures 1 and 2. The 1-VR values for CP in barley and wheat and oil in maize ranged between 0.98–0.99, 0.98–0.99 and 0.95–0.97, respectively. The $SECV$ values for these samples and chemical parameters were low in all cases, but certain differences are apparent. The $SECV$ values for CP in barley and wheat ranged from 0.26 to 0.34 and from 0.25 to 0.36, respectively. Equations obtained for oil in maize yielded a maximum $SECV$ of 0.32 and a minimum of 0.27.

From Figures 1 and 2, some trends concerning the effect of the different mathematical pretreatments can be appreciated. DT transformation with any derivative combination (Equations 3, 16–19) and derivatives with no scatter correction (Equations 8–11) yielded the highest $SECV$s values
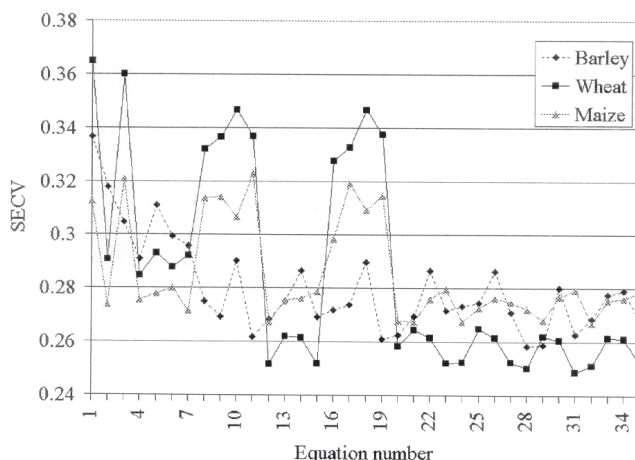

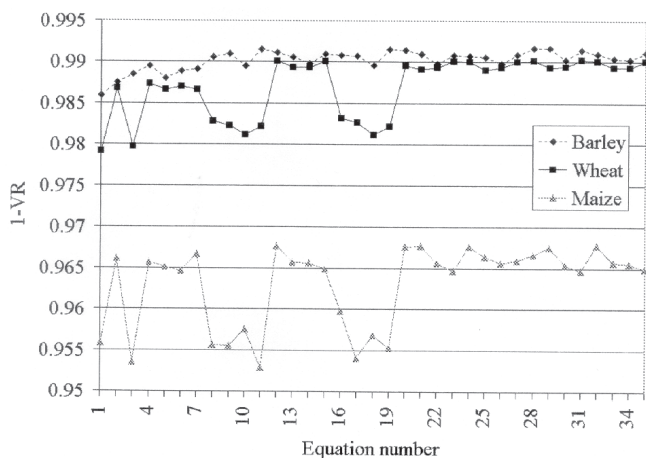**Figure 1. Calibration statistics for all cereals ($SECV$).**

Figure 2. Calibration statistics for all cereals (1-*VR*).

for wheat (0.36, 0.33, 0.33, 0.35, 0.34 and 0.33, 0.34, 0.35, 0.34) and maize calibrations (0.32, 0.30, 0.32, 0.31, 0.31 and 0.31, 0.31, 0.31, 0.32). Best calibrations were obtained for derivatives 1,5,5,1 (all cereals), 2,10,10,1 (barley and wheat) and 1,10,10,1 (maize).

   Once obtained, the equations were evaluated by their ability to be transferred from the instrument on which the equations were developed and which uses reflectance analysis and cups, to the second instrument which uses interactance–reflectance and a fibre optic probe.

   Figures 3 and 4 illustrate the effects of the application of the mathematical pretreatments. The R^2 values for CP in barley and wheat and for oil in maize ranged from 0.65 to 0.88, from 0.32 to 0.78 and from 0.25 to 0.73, respectively. *SED* values for CP in barley and wheat ranged from 0.40 to 5.95 and
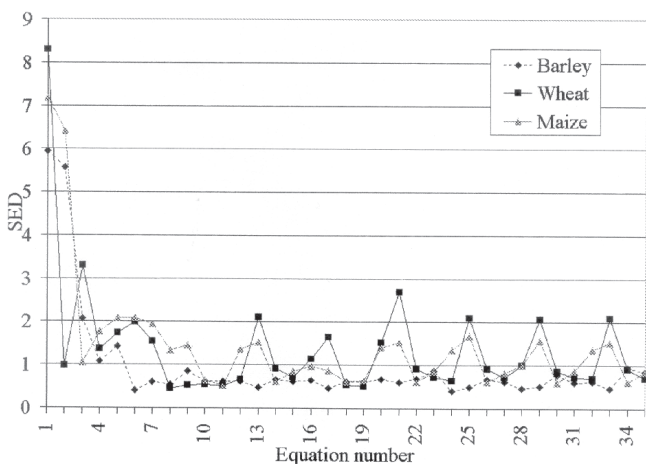

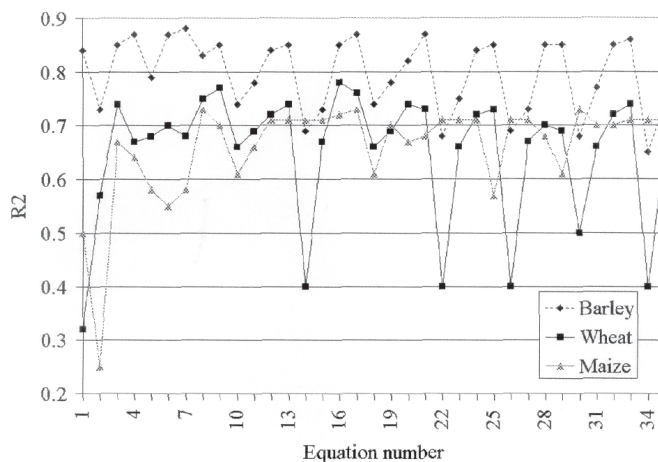**Figure 3. Validation statistics for equation transfer (*SED*).**

Figure 4. Validation statistics for equation transfer (R^2).

from 0.45 to 8.29, respectively. Validation of oil equations for maize gave *SED* values of between 0.52 and 7.17. From these results it can be appreciated that for some combinations of pretreatments, *SED* values for barley, wheat and maize calibrations are similar to *SECV* values. This suggests that the use of pretreatments in calibration development reduces most spectral differences caused by different instruments and different modes of analysis. This effect is more evident when validation statistics are compared for calibrations based on untreated spectra and for the best combination of mathematical pretreatments. For example, *SED* and R^2 values for Equation 1 (no pretreatments) were 5.95 and 0.84 for the barley set, while for Equation 6 (weighted–MSC) they were 0.40 and 0.87, respectively.

The pretreatments used exerted a major effect on validation results. As Figure 3 shows, higher *SED* values were recorded for combinations with derivative 2,5,5,1 for barley (0.61 to 0.95) and 1,10,10,1 for wheat (1.64 to 2.70) and maize (0.87 to 1.67). In terms of R^2 values, first derivatives gave the highest values for wheat and barley, while derivative 2,5,5,1 produced the poorest results (also for maize, when combined with DT or without scatter correction). Strikingly, the use of derivatives without scatter correction gave good results in terms of *SED* and R^2, confirming the results obtained by Fernández *et al.*,[10] except for maize, where R^2 values proved inadequate for second derivatives and *SED* values were high for first derivatives.

From all the information available, it may be concluded that derivative 1,5,5,1 gave better calibration and validation statistics for the equations transferred for barley and wheat, while derivative 2,5,5,1 produced the worst results. The behaviour of maize calibrations was different; while trends of 1-*VR* and R^2 values in relation to derivatives were similar to the other two cereals, *SED* values were lower for derivative 2,5,5,1 than for 1,5,5,1.

Conclusions

The main conclusion of this study is the importance of derivatives for calibration and equation transference statistics. In general, the effect of scatter corrections alone is not as important as the effect of derivatives. Thus, it is recommended that they be used in conjunction with derivatives, selecting the best combination. The use of pretreatments alone is not sufficient to implement a good calibration transfer, based on the quality criteria proposed by Shenk *et al.*,[9] Further work is in progress to combine the use of mathematical pretreatments with other strategies.

Acknowledgements

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