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The transfer of NIR calibrations for undried grass silage from the laboratory to on-site instruments: Comparison of two approaches

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ABSTRACT

As a first step in a project whose aim is to implement near infrared (NIR) analysis of animal feed on the farm, the present work has examined the possibility of transferring undried grass silage calibrations for dry matter, crude protein, and neutral detergent fiber from a dispersive laboratory NIR instrument (Foss NIRSystem 6500) to a diode array on-site NIR instrument (Zeiss Corona 45 visNIR 1.7). Because the samples are complex and heterogeneous and have high humidity levels it is not easy to establish good calibrations, and it is even more of a challenge to transfer them. By cutting the spectral range to 1100–1650 nm and treating with first or second derivative followed by standard normal variate (SNV) scatter correction, it was possible to obtain very similar spectra from the two instruments. To make the transfer, two approaches were tried. Simply correcting the Corona spectra by subtracting the mean difference spectrum from a transfer set met with only limited success. Making a calibration on the Foss using a calibration set of 503 samples with spectra orthogonalized to the all the difference spectra in the transfer set of 10 samples resulted in a successful transfer for all three calibrations, as judged by performance on two prediction sets of size 22 and 29. Measuring 5 replicate subsamples with the Corona allows it to see a similar surface area to that of 3 replicates in the Foss transport cell, and it is suggested that this is an appropriate level of replication for the Corona.

1. Introduction

In some European countries, silages account more than 90% of conserved forages and their importance in ruminant nutrition is increasing [1]. The characterization of grass silage at farm level is important because poor quality silage will have negative nutritional consequences for the animals.

Previous research has demonstrated the possibility of evaluating different nutritive and fermentative parameters on intact undried grass silages using Near Infrared Spectroscopy (NIRS) [2–4]. However, much of this work uses instruments that were designed for the laboratory and would not be robust enough for use on-site at farm level. Recently developed spectrometers, based on array detectors, are potentially useful for process measurement because they are more rugged and better suited to on-line application, even under aggressive conditions [5,6]. Such instruments have been used with raw and milled feedstuffs [5,6]. The aim of the present work was to use one of these robust instruments to measure quality parameters in intact undried grass silage. This is a challenge because intact undried grass silage is heterogeneous, consisting of leaves, stems, and dead material from a wide range of plant species, and has moisture contents ranging from 38% to 87% [3].

The development of NIRS methodologies is not a simple task, because it requires a large number of training samples with reference analyses to establish calibrations [7]. When it is desired to use a new instrument for an application already developed, it would be very inefficient to start again from scratch. Far preferable is to try to use the large NIRS data sets already available to develop calibrations that are able to be transferred to other instruments at-line [8] or on-site [9].

Spectrophotometers, even of the same type, can vary both in wavelength calibration and photometric response. This is due to tolerances, differences in optics, detectors and light sources, changes over time in the instrumental response, etc. [10,11]. When the instruments are of different types, much greater variations can be expected. These differences mean that calibration equations developed on one instrument will not usually perform satisfactorily on another unless they have been deliberately designed or corrected to do so.

There is an extensive literature on calibration transfer; some of it is reviewed by Fearn [10]. Most approaches involve measuring a number of samples on the two instruments concerned to provide information about the spectral differences between the

Abbreviations: CP, Crude Protein; DM, Dry Matter; NDF, Neutral Detergent Fiber; NIR, Near Infrared; PCs, Principal Components; PLS, Partial Least Square; R, Reflectance; SNV, Standard Normal Variation; TOP, Transfer by Orthogonal Projection

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instruments. The spectra from this transfer or cloning set can then be used to develop a correction that maps spectra from one instrument into spectra from the other. In some approaches, such as that of Shenk and Westerhaus [12,13] or the more complicated direct standardization methods [10], this involves regression models. In other cases a very simple correction suffices. Fernandez-Pierna et al. [6] were able to transfer an equation for milled feedstuffs between a laboratory Foss NIRSystem 6500 and an on-site handheld Phazir by simply subtracting from the spectra of one instrument the average spectral difference on the transfer set.

A somewhat different approach involves orthogonalizing the spectra in the calibration set to sources of variability in the transfer set, and then redeveloping the calibration. In transfer by orthogonal projection (TOP) [14] the calibration spectra are orthogonalized to principal components derived from the set of difference spectra for the transfer set. This will produce a calibration robust to the differences between the instruments as observed in the transfer set, though there may be some loss of performance if the orthogonalization also removes some of the signal useful for prediction. Igne et al. [15] compare a number of different orthogonalization methods.

The objective of the present work was to examine the possibility of successfully transferring undried silage calibrations from a dispersive at-line NIR instrument (Foss NIRSystem 6500) to a diode array on-site NIR instrument (Zeiss Corona), comparing the two approaches of mean spectral difference correction [6] and TOP [14] plus mean spectral difference correction.

2. Material and methods

2.1. NIR instruments

A Foss NIRSystem 6500 scanning monochromator (Foss NIRSystem, Silver Spring, MD, USA) with a scanning range of 400–2500 nm at 2 nm intervals was the master instrument. In this study the analysis was carried out using the natural product transport cell, which is a rectangular cell with internal dimensions of 4.7 cm wide, 20 cm long and 4.3 cm deep. The quartz viewing window allows 94 cm^2 of the sample surface area to be irradiated. The spectral data were recorded in reflectance mode ($\log 1/R$) with the WINISI 2 software v.1.05 (Infrasoft International Inc., Port Matilda, PA, USA).

A Corona 45 visNIR 1.7 (Carl Zeiss, Inc.) was the secondary NIR instrument. It is a diode array spectrometer with spectral range from 302 to 1711 nm. A Petri dish with internal dimensions of 9 cm diameter and 2 cm deep was used for sample presentation. The viewing window allows 64 cm^2 of the sample surface area to be irradiated. All values were recorded as $\log (1/R)$, white referencing and dark current measurements were carried out manually. All spectra were recorded using Aspect Plus software version 1.76 (Carl Zeiss, Inc.).

2.2. Samples, NIR analysis and reference data

Set 1, comprising 503 grass silages collected from different farms across northern Spain, was used to develop equations on the Foss instrument for the prediction of nutritive value of grass silages. The silage samples were collected over an extended period from 2002 to 2008 and are representative of the variability encountered in the silage production in wet temperate areas. Aproximately 1 kg of each grass silage sample was firstly well homogenized. In this case, after homogenization each sample was divided into three subsamples and all different subsamples were scanned on the Foss instrument in duplicate. The number of scans per spectrum was set to 32 and the average of all scans was recorded as $\log 1/R$. The final spectrum was the average of the three subsamples.

The samples in set 1 and their spectroscopic scans and reference data existed before the start of the research described here, unlike the other three sets, which were collected and analyzed one set at a time and specifically for this research several years later. The original plan was to use just sets 2 and 3. Set 4, with an increased number of subsamples scanned on the Corona, was added later. The numbers of samples in sets 2–4 were chosen, for reasons of cost, to be as low as was considered reasonable. In each case an attempt was made to include a representative range of samples.

Set 2, comprising 10 intact grass silages, was used to standardize the secondary instrument to the master. Following the protocol detailed for set 1, three different sub-samples of each grass silage were scanned on the Foss instrument in duplicate and the final spectrum was the average of the three subsamples. After Foss scanning, each grass silage sample was re-homogenized and divided on twenty different sub-samples to be scanned into the Corona instrument using an integration time of 100 ms, the final spectrum was the average of all 20. This set intially included 11 samples, but one sample was deleted because its spectrum was very different to all the others.

Set 3, comprising 22 silage samples selected to be representative of the global population, was used as a validation set. These samples were scanned on both instruments as for set 2, except that only two subsamples were scanned on the Corona, instead of 20. This set initially included 26 samples, but four were deleted because their spectra were very different to the remainder.

Set 4, comprising 29 new silage samples collected during 2011, was also used as a validation set. These samples were scanned on both instruments exactly as for set 2. No outliers were deleted from this set.

The same portion of the sample used to collect spectra in both instruments was used for reference data. All samples were analyzed by reference methods in duplicate, after being oven dried at 60 °C for 24 h and ground in a forage mill to pass a 0.75 mm screen. The chemical analysis was performed using traditional analytical methodologies: Dry Matter content (DM) using dry-forced oven (60 °C for 24 h) and corrected by DM at 103 °C during 3 h, Crude Protein (CP) [16] by Kjeldahl analysis, and Neutral Detergent Fiber (NDF) by Van Soest analysis [17]. The reference chemical analysis were performed in an accreditated laboratory under the requirements of ISO/IEC 17025.

2.3. Chemometric tools

In order to develop mathematical and statistical analysis, spectral data collected in both instruments were exported into *csv and imported into the Matlab software v. 7.4 (The Mathworks Inc, US). Subsequent computations and chemometric analysis were carried out with programs written in the Matlab by one of the authors (TF), using functions from the PLS Toolbox v6.01 [18] to carry out the spectral pre-treatment, the cross-validation and the PLS calibration and prediction. The function to implement TOP was written by TF.

2.4. Data analysis

In a preliminary analysis, the spectra for the 10 samples of set 2 were examined. The 10 pairs of spectra corresponding to the same sample on the two instruments were compared, using $\log(1/R)$ and first and second derivative spectra. The derivatives, here and later, were calculated using a Savitzky–Golay filter with a third order polynomial and a 15-point window. The effect of SNV

treatment was also studied, with the order of application being derivative then SNV when both were used.

Following this preliminary analysis, the spectral range for both instruments was cut to 1100–1650 nm, and the log(1/*R*) Foss spectra for all four sample sets were converted to Corona wavelengths using linear interpolation. This was based on the wavelengths output by the instrument manufacturers' software. Except for one case noted below, all the subsequent calculations, including that of derivatives, started with these truncated and converted spectra.

Next, PLS calibrations for DM, NDF and CP were developed using the truncated and converted Foss spectra on the calibration set (set 1), trying first and second derivatives, with and without SNV, and choosing both data pretreatment (order of derivative and use or not of SNV) and numbers of factors using leave-one-out cross-validation. For comparison purposes these calibrations were repeated using the full range and original wavelengths of the Foss spectra, fixing the pretreatment at that chosen for the truncated and converted spectra but re-optimizing numbers of factors using leave-one-out cross-validation.

The first transfer approach to be investigated was the simple one of correcting the Corona spectra by subtracting from them the mean difference between the Foss and Corona spectra for the 10 samples of set 2 [6]. To investigate the performance of this approach, the calibrations developed as described above on the truncated and converted Foss spectra were used to predict all three reference values for sets 3 and 4, using spectra from each instrument and with the mean difference correction applied to the Corona spectra.

The alternative approach of TOP [14], was then investigated. This requires that the calibrations be remade with the calibration spectra treated by orthogonalizing them to principal components (PCs) derived from the 10 difference spectra, Foss spectrum minus Corona spectrum, for the samples of set 2. The three calibrations were refitted to set 1 after orthogonalizing its spectra to 9 such PCs, the maximum number available with 10 samples, again trying first and second derivatives without and with SNV, and optimizing both this choice and that of the number of factors using leave-one-out cross-validation. One non-obvious issue in deriving these calibrations concerns the interaction between the orthogonalization and the application of SNV. Because the latter is nonlinear, it does make a difference in which order these are applied, and both orders were tried. The resulting calibrations

Table 1
Mean values, standard deviations and ranges for chemical composition (%) of undried grass silage calibration (set 1), cloning (set 2) and validation sets (sets 3 and 4).

	DM	CP	NDF
Set 1			
Maximum	61.87	8.60	40.01
Minimum	13.00	1.57	6.82
Mean	29.71	3.83	18.03
Standard deviation	8.34	1.28	5.72
Set 2			
Maximum	41.19	6.15	23.27
Minimum	18.99	2.05	11.56
Mean	29.36	3.68	17.46
Standard deviation	8.07	1.25	4.15
Set 3			
Maximum	52.57	8.23	27.99
Minimum	18.94	2.12	8.93
Mean	34.15	4.78	18.02
Standard deviation	9.99	1.43	5.88
Set 4			
Maximum	63.15	8.35	49.10
Minimum	20.36	2.11	12.47
Mean	36.89	4.72	23.82
Standard deviation	11.93	1.69	9.28

DM: Dry Matter; CP: Crude Protein and NDF: Neutral Detergent Fiber.

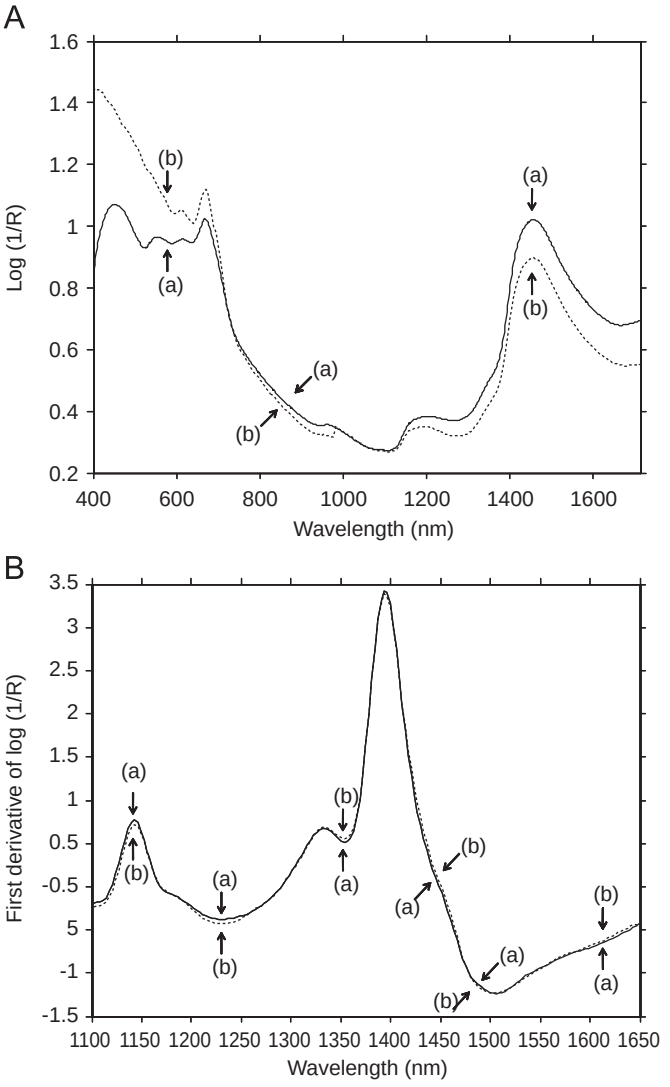

Fig. 1. Mean spectra for the transfer set (set 2) on the two instruments.(A) Raw log(1/*R*) spectra with no pretreatment, using the full overlapping spectral range and (B) First derivative spectra with SNV treatment, restricted to the range 1100–1650 nm. In both plots the solid line (a) is the Foss and the dotted line (b) is the Corona.

Table 2
Root mean squared errors of cross-validation (RMSECV) for Foss calibrations on set 1 and *nf* is the number of PLS factors in the calibration.

Spectral range(nm)	DM	CP	NDF
400–2498	1.53 (*nf*=9)	0.49 (*nf*=10)	1.59 (*nf*=10)
1100–1650	1.43 (*nf*=7)	0.51 (*nf*=12)	1.54 (*nf*=7)
1100–1650*	1.65 (*nf*=8)	0.53 (*nf*=10)	1.58 (*nf*=10)

DM: Dry Matter; CP: Crude Protein and NDF: Neutral Detergent Fiber. The DM and NDF calibrations use first derivative spectra, the CP calibrations use second derivative and all are SNV treated.

* Spectra orthogonalised to cloning set differences.

were used to predict reference values for sets 3 and 4, using spectra from each instrument. The Corona spectra were corrected by subtracting the mean spectral difference for set 2 before making these predictions, as well as being pre-treated in exactly the same way as the calibration spectra. Thus TOP was applied as well as the mean difference correction, not instead of it.

To investigate the effect of scanning different numbers of replicate subsamples on the Corona, the predictions for set 4 were repeated using the averages of the first k subsamples, for values of k from 2 to 20.

Table 3
Root mean squared errors of prediction (RMSEP) for sets 2–4 using both Foss and Corona instruments, with Corona spectra corrected by subtraction of mean difference spectrum.

	DM	CP	NDF
Set 2			
Foss	1.33	0.37	1.00
Corona	1.83	5.74	2.34
Set 3			
Foss	1.88	0.50	1.44
Corona	3.49	6.98	3.16
Set 4			
Foss	2.65	0.62	2.47
Corona	2.19	9.77	3.49

DM: Dry Matter; CP: Crude Protein and NDF: Neutral Detergent Fiber. These use the calibrations in the second row of Table 2.

3. Results and discussion

The means, standard deviations and ranges for chemical composition of grass silage in set 1 (calibration) and sets 2 (cloning), 3 and 4 (validation) are given in Table 1. The wide range and the standard deviation for dry matter, crude protein and neutral detergent fiber confirm the wide diversity of grass silage involved in the calibration set.

Fig. 1(A) shows the mean log(1/R) spectra for set 2 in the common spectral range of the two instruments. In this figure can be seen very large differences between the instruments in the visible region, a discontinuity in the Corona spectrum at 978 nm, and, barely visible, a discontinuity in the Foss spectrum at 1100 nm. Not visible from this plot, but seen when individual spectra are plotted, there are variable differences between the instruments above about 1650 nm. These considerations motivated the choice of 1100–1650 nm as a working range.

Fig. 1(B) shows the mean first derivative, SNV treated, spectra for set 2 in the range 1100–1650 nm. These spectra match fairly well between instruments, as do the second derivative, SNV treated, spectra (not shown). In particular the wavelengths of the two instruments seem to be very closely aligned, the peaks in the same positions.

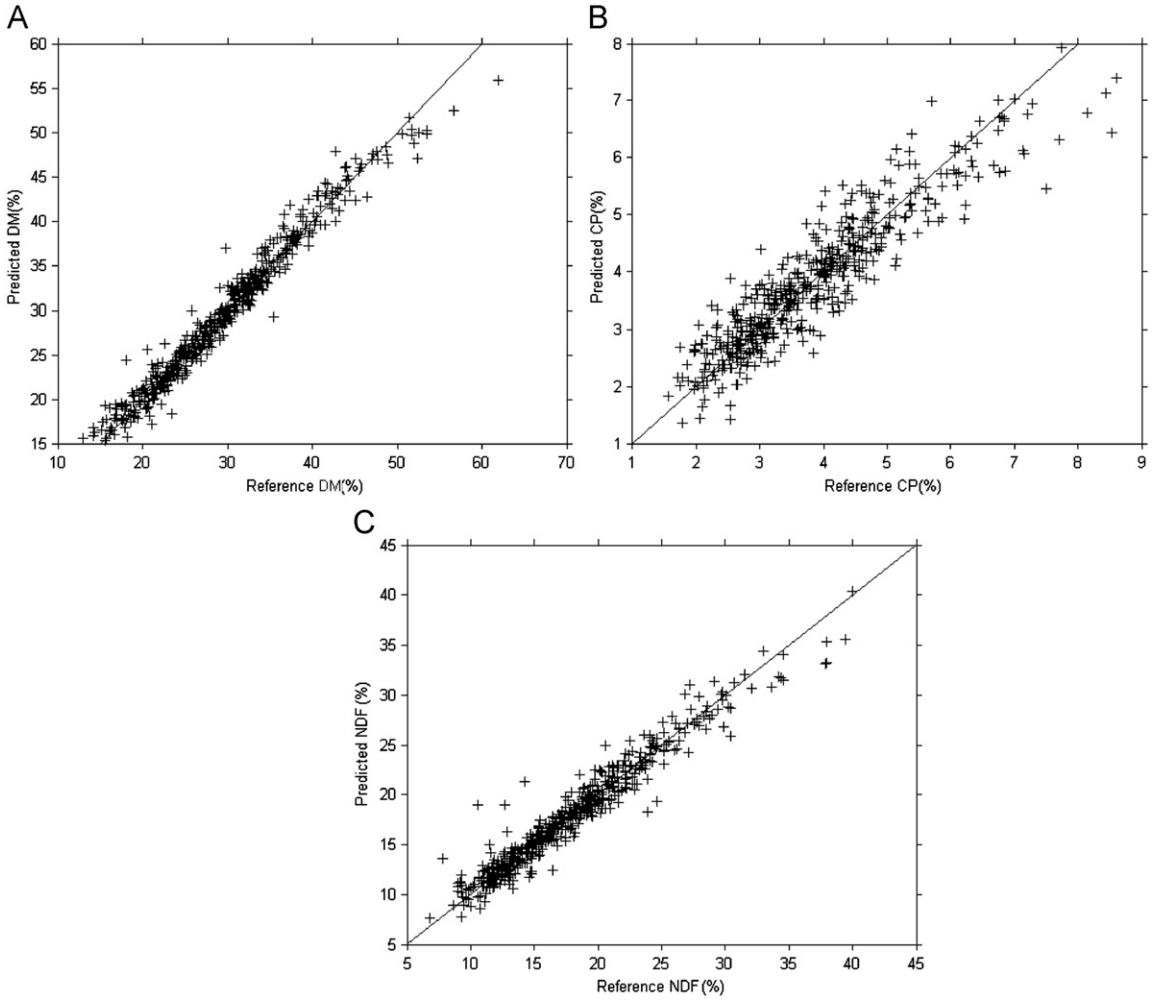

Fig. 2. Relationship between predicted and reference values obtained with NIR calibrations to transfer on intact grass silage: (A) Dry Matter (DM); (B) Crude Protein (CP) and (C) Neutral Detergent Fiber (NDF).

The RMSECV values for the PLS calibrations for DM, NDF and CP developed on the truncated and converted Foss spectra for set 1 are shown in row 2 of Table 2, as are the numbers of PLS factors. The calibrations for DM and NDF used first derivative, that for CP used second derivative, all three used SNV. For comparison, the RMSECV for calibrations using the same data pre-treatment but the full Foss wavelength range are shown in row 1. Cutting the wavelength range did not appear to affect performance, although one cannot be sure that other pretreatments or intermediate choices of range might not have performed better.

Table 3 shows the results of using these calibrations to predict sets 2–4 using spectra from both instruments and with the simple mean difference correction applied to the Corona spectra. The transfer worked reasonably well for DM, worse though not too badly for NDF, and failed completely for CP. The CP calibration uses second derivative and a larger number of factors than the other two. Both of these may contribute to the failure of the simple approach to calibration transfer.

Row 3 of Table 2 shows the RMSECV for Foss calibrations using spectra orthogonalized to all 9 PCs derived from the difference spectra for set 2. There does appear to be some slight loss of performance, but there is no serious deterioration, so it was decided to use these calibrations and not to investigate the effect of reducing the number of PCs below 9. Fig. 2 shows the NIR-predicted versus reference plots for all three calibrations. The DM and NDF calibrations look very good. The CP calibration has a suggestion of curvature and becomes noisy for high values, but is acceptable.

Table 4 shows the results of using these calibrations to predict the reference values for sets 2–4. There is a general improvement compared with Table 3, and a dramatic improvement in the results for the CP calibration, which now transfers very well. The predictions for the two instruments on set 2 are identical because the TOP procedure, combined with subtracting the mean difference, makes them so. Given the heavy involvement of this set in the calibration, these 'prediction' results are probably not very meaningful. Comparing sets 3 and 4, the Foss performs similarly on the two sets but the Corona is much worse on set 3 than on set 4. The reason is that the Corona only scanned two subsamples in set 3, but 20 subsamples in set 4. The effect of this

Table 4
Root mean squared errors of prediction (RMSEP) for sets 2–4 using both Foss and Corona instruments, using TOP and with Corona spectra corrected by subtraction of mean difference spectrum.

	DM	CP	NDF
Set 2			
Foss=Corona	0.92	0.38	1.09
Set 3			
Foss	2.18	0.56	1.64
Corona	3.66	1.29	2.79
Set 4			
Foss	2.11	0.41	2.16
Corona	1.86	0.55	2.17

DM: Dry Matter; CP: Crude Protein and NDF: Neutral Detergent Fiber. These use the calibrations in the final row of Table 2.

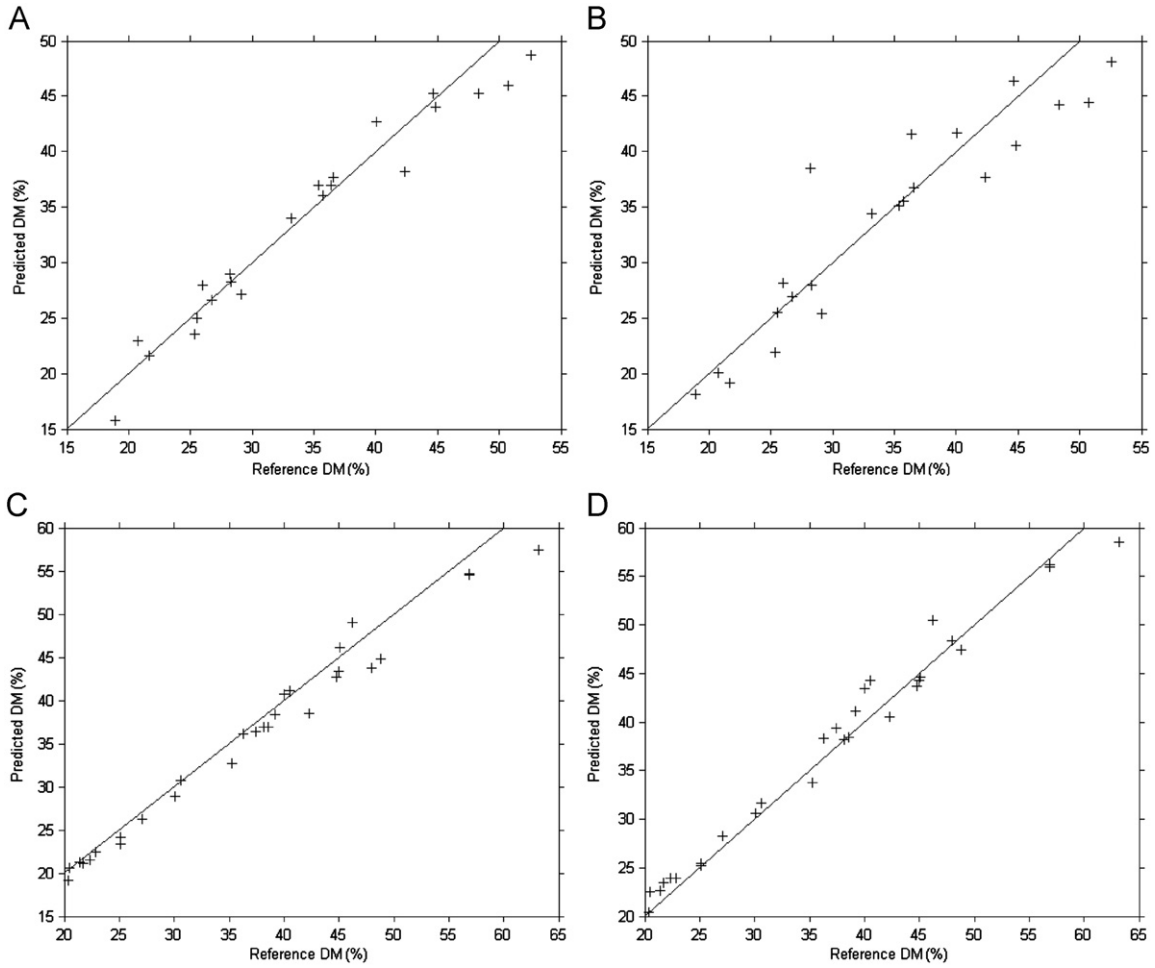

Fig. 3. Dry Matter (DM) validation results for the master (Foss) and secondary (Corona) instruments: (A) Foss-set 3; (B) Corona-set 3; (C) Foss-set 4 and (D) Corona-set 4. Set 3 ($N=22$): final spectra is the average of two sub-samples each scanned in duplicate and set 4 ($N=29$): final spectra is the average of 20 subsamples.

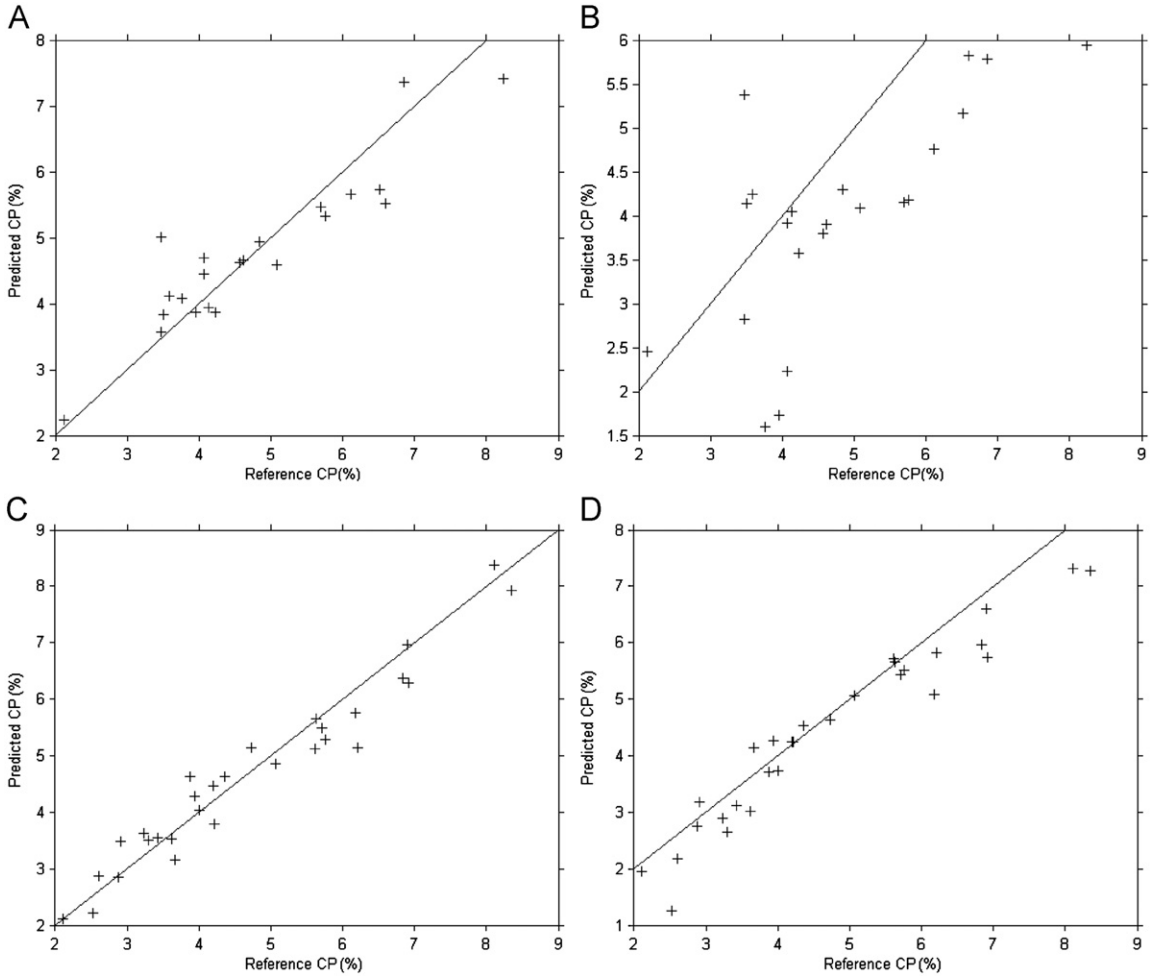

Fig. 4. Crude Protein (CP) validation results for the master (Foss) and secondary (Corona) instruments: (A) Foss-set 3; (B) Corona-set 3; (C) Foss-set 4 and (D) Corona-set 4. Set 3 (N=22): final spectra is the average of two sub-samples each scanned in duplicate and set 4 (N=29): final spectra is the average of 20 subsamples.

can be seen in Figs. 3–5, which show the predictions for the two instruments for sets 3 and 4 for all three parameters. The extra scatter in the Corona predictions for set 3 can clearly be seen. It is also apparent, from the very similar patterns in the pairs of plots, that the instruments are making very similar predictions.

Trying both options for the order of spectral treatments showed that the calibration and especially the transfer were both better if the orthogonalization was done first, so the order of treatments in the results presented was derivative, orthogonalization, SNV. That this order works best is unfortunate, because it means the Corona spectra need to be othogonalized before being used for prediction, something that would not have been necessary had the SNV preceded the orthogonalization.

Examining the RMSEP results for the Corona predictions on set 4 using fewer than 20 subsamples showed, as one would expect from statistical considerations, improvements in performance that tailed off rapidly as the number of subsamples increased. With 5 subsamples the RMSEP values were 2.14, 0.59 and 2.61 for DM, CP and NDF respectively, a little worse than those in the bottom row of Table 4 but still acceptable. With 3 subsamples on the Foss, this instrument sees $3 \times 94 = 282$ cm^2 of sample surface. To get the same area with the Corona requires between 4 and 5 subsamples, so the correspondence seems about right.

Employing the same instruments involved in this study (Foss NIRSSystem 6500 and Zeiss Corona), previous researchers [2,19] have transferred NIR calibrations using the Shenk and Westerhaus patented algorithm [13] to predict nutritive parameters on intact grass silages and feed compounds, developing the cloning matrix with five samples. However these researchers found that an additional step was necessary, involving the addition of spectra analyzed in both instruments to the calibration set. This performs a similar function to TOP, in that the presence in the calibration set of pairs of spectra whose differences should predict zero penalizes the contribution to the calibration of the dimensions spanned by these differences.

4. Conclusions

This study has established that it is possible to successfully transfer, using TOP, calibrations to predict the chemical composition of intact grass silages from an at-line (Foss) to an on-site (Corona) NIR instrument. In particular neither cutting the spectral range of the monochromator nor pre-treating its spectra by orthogonalizing to spectral differences between the two instruments seriously damaged the predictive performance of the Foss calibrations. These Foss calibrations orthogonalized using TOP could be transferred to the Corona with the aid of a correction for mean spectral difference, to give acceptable results on prediction samples. Measuring five replicate subsamples with the Corona allows it to see a similar surface area to that of three replicates in

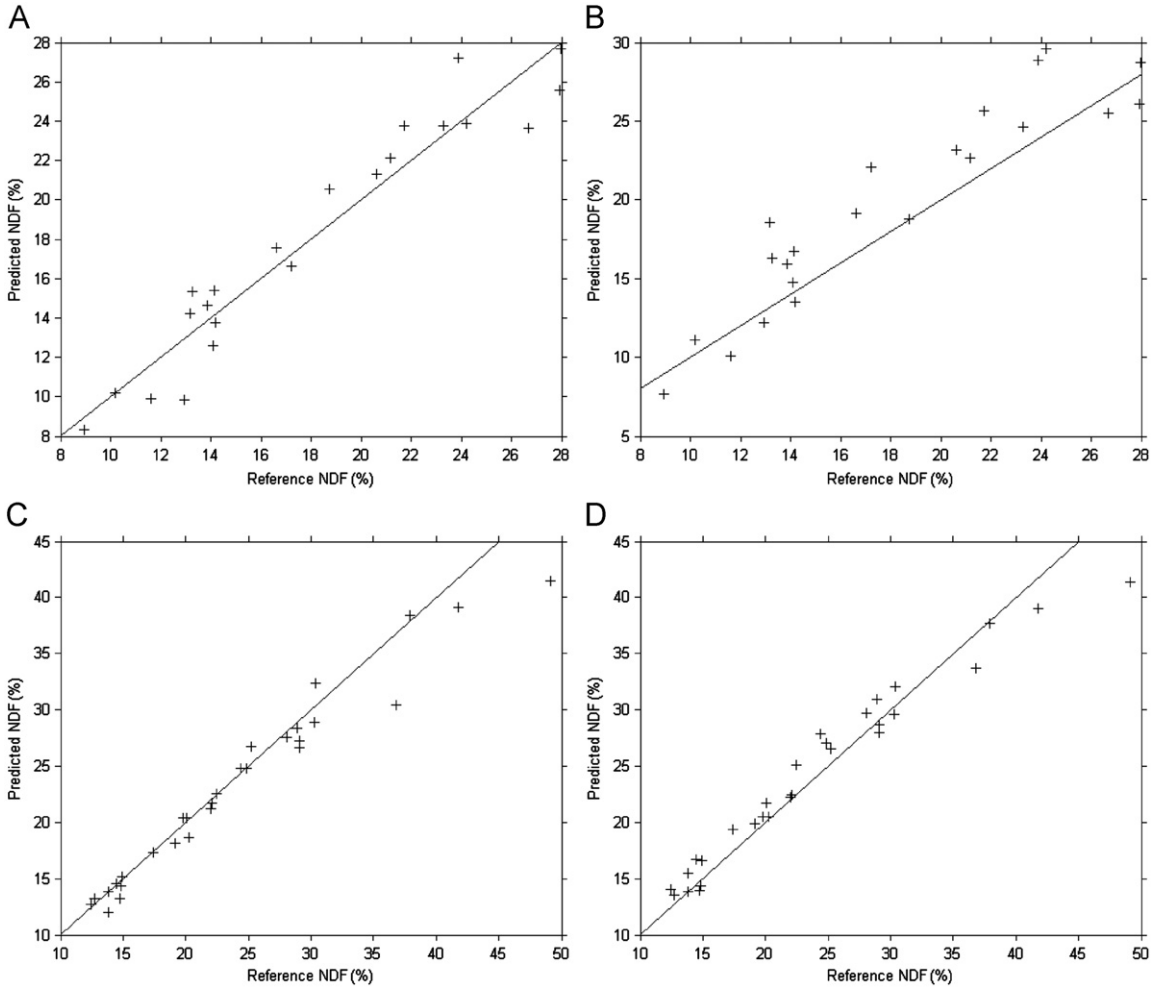

Fig. 5. Neutral Detergent Fiber (NDF) validation results for the master (Foss) and secondary (Corona) instruments: (A) Foss- set 3; (B) Corona-set 3; (C) Foss-set 4 and (D) Corona-set 4. Set 3 ($N=22$): final spectra is the average of two sub-samples each scanned in duplicate and set 4 ($N=29$): final spectra is the average of 20 subsamples.

the Foss transport cell, and it is suggested that this is an appropriate level of replication for the Corona.

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