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Improving the Transfer of Near Infrared Prediction Models by Orthogonal Methods

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1 **Improving the Transfer of Near Infrared Prediction Models by**

2 **Orthogonal methods**

3

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9

10 **Abstract**

11 Eight calibration transfer methods based on the removal of orthogonal signal were compared for the
12 standardization of whole soybean protein and oil models. Dynamic orthogonal projection (DOP),
13 transfer by orthogonal projection (TOP), error removal by orthogonal subtraction (EROS), orthogonal
14 signal correction (OSC), and orthogonal projections to latent structures (O-PLS) as well as the
15 modification and extension of some of these methods were compared in the transfer of models in intra
16 and inter brand situations using two Foss Infratecs and two Bruins OmegAnalyzerGs. For each brand, a
17 master was designated and its models transferred onto the second unit of its network and the two units
18 of the second brand. Calibration models were transferable from brand to brand with similar or better

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1 precision than when each instrument was calibrated on its own calibration set (for Infratec 1229, the
2 relative predictive determinant (RPD) increased in intra and inter-brand calibration transfer situations
3 from 10.42 to 11.45 and 10.57, with DOP and EROS respectively) . Performance of each method was
4 different across parameters, instruments, and validation sets. DOP modifications on the determination
5 of the difference matrix showed promising results while TOP and EROS extensions to include
6 variability specifically present in certain crop years did not bring any beneficial effects.

7

8 *Keywords:* Orthogonal signal correction (OSC), Orthogonal PLS (O-PLS), Dynamic orthogonal
9 projection (DOP); Transfer by orthogonal projection (TOP); Error removal by orthogonal subtraction
10 (EROS); near infrared spectroscopy

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1 **1. Introduction**

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3 Near infrared spectroscopy (NIRS) is a fast, non destructive, and inexpensive analytical tool
4 involving limited or no sample preparation. For the past thirty years, NIRS has been used in numerous
5 applications from the screening and quality control of food and feed products [1,2,3] to pharmaceutical
6 and chemical processes control [4,5]. Near infrared spectra are the results of the absorption of
7 overlapping bands from different chemical families requiring information extraction from complex and
8 highly collinear databases. Chemometrics methods are used to build calibration models describing the
9 relationship between the spectral data (**X** matrix) and the dependent variable of interest (**Y** matrix)
10 measured by reference method.

11 One of the factors impacting the development and the use of regression models is the lack of
12 robustness [6]. “The robustness/ruggedness of an analytical procedure is a measure of its capacity to
13 remain unaffected by small, but deliberate variations in method parameters and provides an indication
14 of its reliability during normal usage” [7]. The robustness of a model can be stressed over time by
15 changes not only in the sample (temperature, composition, and presentation), but also by instrumental
16 disturbances, aging, and by inter-instrument variability that impacts transfer ability to other units.

17 Several correction strategies have been implemented to cope with the influence of these
18 external parameters. Optical methods aim at modifying the spectra collected on secondary units to
19 match those collected by the master unit. The model developed on the master unit is then used to
20 perform predictions on the secondary units. Direct and piecewise direct standardization [8] and the
21 Shenk and Westerhaus patented algorithm [9] are some examples of optical methods. These techniques
22 use a set of transfer samples to perform the spectral matching.

1 A second approach is to adapt predictions using a slope and an offset or a simple bias
2 correction. These parameters are obtained by a linear regression between predictions made on the
3 secondary unit and the reference values on a selected set of transfer samples by the same model. This is
4 a widely used technique. Most, if not all, instrument firmware or software support these corrections.

5 While the two approaches did not aim at enhancing model robustness but rather bypass external
6 parameters, a third approach, commonly named robust models, creates models themselves able to deal
7 with this external variability. There are three ways to develop robust models: (i) optimizing calibration
8 sample set, (ii) optimizing the feature selection, and (iii) preprocessing the signal.

9

10 *1.1 Optimization of sample sets*

11

12 For a calibration to predict a wide variability of experimental conditions, it is possible to
13 develop exhaustive calibration sets. These sets contain samples scanned at different temperatures, with
14 different sample presentations, on different instruments, and with a large variety in genetic and
15 environmental sources [10]. During the calibration process, the influence of external parameters is
16 automatically built into the prediction model. The model may present lower predictive abilities, but is
17 able to give reliable predictions in conditions where more restrictive models would be inaccurate.

18 An alternative to exhaustive calibration models is local modeling. Local chemometrics regroup
19 regression methods that select among the pool of samples available in the calibration set samples that
20 are closer to the one to predict. Local methods may perform better and be more robust than exhaustive
21 models, but have the disadvantage of not presenting a fixed set of regression coefficients. Algorithms
22 exist for local modeling such as locally weighted regression [11,12], LOCAL [13], and CARNAC-D
23 [14,15].

1 *1.2 Feature selection*

2
3 Robustness can also be achieved by selecting, among the variables available, only those
4 relevant to the parameter of interest. Variable selection has been successfully applied to NIRS by
5 exhaustive search, simulated annealing [16], genetic algorithms [17,18,19,20], interval-partial least
6 squares [21], and particle swarm optimization [22]. For model transfer, the search for isonumeric
7 wavelengths – not subject to axis shift – was also implemented [23]. In the present study, the issue of
8 correspondence of wavelength axis was not addressed since both brands show the same range and
9 resolution. The reduction of the dimensionality of the \mathbf{X} matrix results in more parsimonious models
10 [24], including less noise, and less subject to overfitting.

11 12 *1.3 Signal pretreatment*

13
14 Another possibility to achieve model robustness is to use preprocessing methods. Smoothing
15 (Savitzky-Golay smoothing and derivatives [25]), scattering correction (standard normal variate (SNV)
16 [26], and multiplicative scatter correction [27]) has been widely used to remove noise and other
17 unwanted signal.

18 A new approach to signal pretreatment are the orthogonal methods. They are based on the
19 theory that the column space of the \mathbf{X} matrix (all possible linear combinations of column vectors) is
20 “the sum of two subspaces, among which only one contains information useful for the model “[28].
21 There exists two ways of estimating the “uninformative” subspace: (i) by using the space orthogonal to
22 the \mathbf{Y} matrix and (ii) by estimating the space where external factors have a significant influence. The

1 former can be considered as being part of the calibration model development while the latter is similar
2 to pretreatment methods.

3 The first approach contains techniques such as orthogonal signal correction (OSC) [29] and
4 orthogonal projections to latent structures (O-PLS) [30]. These two techniques remove, from the \mathbf{X}
5 matrix, factors that are not correlated to the \mathbf{Y} matrix. Loadings of these factors are later subtracted
6 from the \mathbf{X} matrix before calibration development. These techniques require the orthogonalization of
7 every sample to be predicted in the future.

8 The second approach estimates the space in which external parameters are and removes it from
9 the \mathbf{X} matrix. External parameter orthogonalisation (EPO) [28], independent interference reduction
10 (IIR) [31], transfer by orthogonal projection (TOP) [32], dynamic orthogonal projection (DOP) [33],
11 and error removal by orthogonal subtraction (EROS) [34] are methods that estimate interferences by
12 using a set of samples measured in the different conditions of interest to create a difference matrix
13 representing external factors. The difference matrix between interfering and non-interfering conditions
14 is decomposed in principal components and the first few loadings are removed from \mathbf{X} . A calibration
15 model is developed with the new preprocessed \mathbf{X} matrix. The advantage over OSC and O-PLS methods
16 is that new samples do not need to be orthogonalized. Regression coefficients reflect the removal of
17 external interferences from the calibration data. The correction is embedded into the model, which will
18 not take into account the perturbation (which can either be or not present) in the new spectra to be
19 predicted.

20

21 Due to the novelty of these methods, the literature does not provide extensive results. Their
22 performance in calibration transfer procedure has not been studied. In this study, we have evaluated the
23 ability of orthogonal projection techniques to enhance model transferability in a network of four near

1 infrared units from two brands. To evaluate their effect, validation results were compared with
2 piecewise direct standardization, exhaustive calibration, and post-regression slope and bias correction.
3

4 **2. Theory**

5
6 Orthogonal signal correction and O-PLS, for the category of orthogonal methods using the \mathbf{Y}
7 matrix, as well as DOP, TOP, and EROS for techniques using only the \mathbf{X} matrix, were evaluated. The
8 subtraction of the influential subspace from the original \mathbf{X} matrix (X_0) is performed by

$$9 \quad X_0^* = X_0 - C \quad (1)$$

10 where \mathbf{C} is a correction matrix. X_0^* is then used to develop prediction models. The difference between
11 the various orthogonal techniques depends on the way \mathbf{C} is calculated.
12

13 *2.1 Orthogonal signal correction*

14
15 Orthogonal signal correction uses the NIPALS algorithm [35] to decompose \mathbf{X} into scores t (by
16 principal component analysis (PCA)). These scores are orthogonalized to \mathbf{Y} to obtain t_{new} and a weight
17 factor w is calculated ($w = X_0^- t_{new}$) with X_0^- being a generalized inverse. New scores t are determined
18 with $t = Xw$ and the loading vector p is estimated ($p^T = t^T X_0 / (tt_{new})$). The correction matrix \mathbf{C} is
19 finally estimated by $C = tp^T$. The operation can be repeated until the desired number of corrections has
20 been applied to X_0 . More details about OSC algorithm can be found in Ref. [29].
21

2.2 Orthogonal projections to latent structures

Orthogonal projections to latent structures uses also the NIPALS algorithm to obtain weight

factor w and loading factor p necessary to calculate an orthogonal weight factor w_{ortho}

$(w_{ortho} = p - [w^T p / (w^T w)] w)$. w_{ortho} is then used to approximate orthogonal scores

$(t_{ortho} = X_0 w_{ortho} / (w_{ortho}^T w_{ortho}))$ which are used to determine orthogonal loadings

$(p_{ortho}^T = t_{ortho}^T X_0 / (t_{ortho}^T t_{ortho}))$. Similarly to OSC, the correction matrix is estimated by $C = t_{ortho} p_{ortho}^T$.

The projection can be repeated until satisfaction using X_0^* to replace X_0 . Ref. [30] provides more

details about the O-PLS decomposition.

2.3 Transfer by orthogonal projection

Transfer by orthogonal projection uses standards measured on both units (or in different conditions, for instance, temperature) to determine an interference matrix. Transfer samples are run on both instruments. The difference between the same samples scanned on different instruments is used to form a matrix D . A principal component analysis is performed on D and the first k loadings are used to form the matrix P_k . The influential space is then calculated using $X_0 P_k^T P_k$. Equation 1 becomes

$$X_0^* = X_0 (I - P_k^T P_k) \quad (2)$$

where I is the identity matrix. TOP can be extended to more than two instruments [32].

2.4 Error removal by orthogonal subtraction

Error removal by orthogonal subtraction presents again a different way to calculate C . A difference matrix D is obtained in the same way as in TOP; but instead of calculating P based on the first PCA loadings of D , the PCA decomposition is performed onto the matrix W which represents the variability between replicate measurements. W is defined as $W = \sum_{i=1}^m (D_i D_i^T / (r - m))$ where D_i is the difference matrix for sample i , r the pooled within-sample covariance matrix of the spectra and m is the number of samples.

2.5 Dynamic orthogonal projection

In calibration transfer situations, a few spectra collected on the secondary unit only are used to create virtual standards. They are created using a kernel function based on the calibration set (X_0 and Y_0 matrices) and the reference value of samples collected on secondary unit (Y_t matrix). Virtual standards are estimated by $\hat{X}_t = AX_0$ with $a_{ij} = F_{y_{ii}}(Y_{0j})$ where $F_{y_{ii}}$ is a kernel function centered on y_{ii} for the i^{th} sample and the j^{th} variable. The difference matrix D is estimated by taking the difference between X_t and \hat{X}_t . A PCA is done on D and the first k loadings are used to form the matrix P . Orthogonalization is performed similarly as in TOP (equation 2). The kernel function used is a Gaussian kernel. A detailed discussion of the optimization of the method is provided in Ref. [33].

3. Material and methods

3.1 Sample, spectral collection and reference analysis

Approximately 630 whole soybean samples collected and scanned during crop years 2002 to 2005 were included in the calibration set. The network of instruments was composed of two Foss Infratec Grain Analyzers (1229 and 1241 – s/n 553075 and 12410350 respectively) (FOSS North America, Eden Prairie, MN, USA) and Bruins OmegAnalyzerGs (s/n: 106110 and 106118) (Bruins Instruments, Puchheim, Germany). Both are transmittance instruments with a spectral range from 850 nm to 1048 nm at 2 nm increment. OmegAnalyzerGs scan 741 wavelengths from 730 nm to 1100 nm. A software option reduces the spectra to the same 100 data points as the Infratec units. A pathlength of 30 mm was used.

Samples were run at room temperature. Each sample was run simultaneously on the four instruments. In the final database, the number of samples was not the same for all four units: a sample identified as an outlier for one unit could be reasonably predicted by another unit. Also, not all instruments had the possibility to scan smaller samples without changing the number of subscans. This situation was considered closer to a field experiment than reducing to exactly the same samples in all four calibration sets.

Protein content was determined by combustion (AOAC 990.03), oil content was determined by ether extract (AOCS Ac 3-41), both by Eurofins Scientific, Inc., Des Moines, IA, USA. Summary statistics for the calibration sets are presented in Table 1.

3.2 Validation sets

Two validation sets were used. The first set contained a “known” variability. It included 20 samples selected over years (up to 2005) by the Grain Quality Laboratory, Ames, IA, USA. These samples were not part of the calibration set and were selected/updated annually to be good predictor samples for the slope and bias standardization procedure of the laboratory’s instruments. These samples had four or more reference measurements per parameter. The second set was created using forty samples from crop year 2006 and came from an origin intentionally different from the samples present in the calibration set (genetically and geographically). This set presented the prediction models with “unknown” variability. Scan conditions and determination of the reference values were similar to samples in the calibration set. Summary statistics for the validation sets are also presented in Table 1.

3.3 Calibration procedure

(i) Spectral pretreatment and outlier detection

Raw spectral data were corrected for baseline and scattering effect by calculating their second derivative spectra using the Savitzky-Golay algorithm (25-point window and 3rd-order polynomial). Each sample was normalized to the sum of the absolute value of absorbance for all variables (wavelength) for the given sample. Each variable was scaled to zero mean and unit standard deviation. The detection of outliers was performed on the fully pretreated spectra by removing from the calibration set samples presenting a Hotelling T^2 and a Q residual value larger than the 95% confidence interval.

1 (ii) *Calibration and validation procedures*

2 Partial least squares (PLS) regression was used to develop all prediction models. In PLS, the
3 original matrix is compressed into latent variables that maximize the covariance between the reference
4 values and all possible linear functions of the spectral data [36]. The number of latent variables was
5 optimized using leave one out cross validation.

6
7 (iii) *Model evaluation and comparison parameters*

8 The performance of the prediction models was evaluated on the two validation sets. Relative
9 predictive determinant (RPD) was used to measure precision. RPD is the ratio of standard deviation of
10 the reference values to the standard error of prediction (SEP_c) – the standard deviation of the
11 differences between predicted and reference values of the validation set corrected for bias. RPD
12 represents how well the calibration model predicts the validation set and is evaluated with the scale
13 provided by Williams [37]. Bias, the average difference between predicted and reference values,
14 measured the predictive fidelity of the models.

15
16 3.4 *Selection of transfer set*

17
18 For orthogonal methods using transfer samples (TOP, EROS, and DOP), a set of twenty
19 standardization samples was created. In order to choose a representative and well predicted set of
20 samples, the following procedure was done. Ten subsets of twenty samples each were randomly
21 selected from the calibration set. Their protein, and oil concentration ranges were checked to match the
22 ranges of the remaining calibration samples. A new random subset was created if the ranges were not
23 adequate. A calibration for each parameter was developed without one subset at a time and the subset

1 taken apart was predicted with the calibrations models (similar to block cross validation). The subset
2 that presented the lowest SEP_c and bias for both parameters (equally weighted) was chosen as the
3 standardization set. It was then removed from the calibration set.

5 *3.5 Experimental*

6
7 After calibrating each instrument on its own calibration set to determine benchmark results, a
8 master unit was identified for each instrument brand network. Models of these master units were used
9 to evaluate the ability of the five selected orthogonal methods to transfer these calibration models in
10 intra and inter-brand situations. Piecewise direct standardization (PDS) (tested with window size of 1,
11 3, 5, and 7), slope and bias, and exhaustive calibration models including the spectral data from both
12 masters units were compared to the performances of orthogonal methods. More details about these
13 common standardization methods can be found in Ref. [38].

14 Since samples in the calibration set were collected over four years, an attempt to model
15 instrumental changes over those years was done. Instrument aging differently, if the inter-annual
16 variability could be removed, the transfer of calibration models might be made easier. A set of twenty
17 samples scanned every year by the Grain Quality Laboratory for control purposes, different from
18 calibration, validation, and standardization sets, was used to perform TOP and EROS. These samples
19 had the particularity to have been scanned the same years calibration samples were collected and
20 reflected instrumental variations over the years. They were used to form the difference matrix \mathbf{D} . They
21 were called TOP 4years and EROS 4years.

22 A modification to DOP was also evaluated. Instead of taking into consideration only the
23 parameter of interest (protein or oil) when creating the virtual standards, both parameters were used

1 either at the same time or one after the other to form the matrix D . They were respectively named DOP
2 2y block and DOP 2y sequential. In DOP 2y block, the D matrix was formed by concatenating
3 difference spectra for protein and for oil while in DOP 2y sequential, the calibration set was first
4 orthogonalized for differences in protein, then for differences in oil. This was an attempt to increase the
5 robustness of models by considering more variability than present for one parameter alone.

6 Methods optimization (choice of the number of PLS latent variables, of loadings to include in
7 P , and of the width of the kernel function for DOP) was done by using the set of parameters that best
8 predicted both validation sets. A set of coefficients may have performed better on one set than on
9 another, but this option was a way to limit overfitting and enhance robustness. Table 2 summarizes the
10 different standardization compared in this study.

11 All calculations were performed on MATLAB R2007b (The MathWorks, Natick, MA). PLS
12 models as well as DS and PDS standardization methods were developed with the PLS_toolbox 4.2.1
13 (Eigenvector Research, Wenatchee, WA).

14

15 **4. Results and discussion**

16

17 *4.1 Benchmark results*

18

19 Table 3 presents the validation results when each instrument is calibrated on its own calibration
20 set. Fearn [39] presented a technique originally proposed by Pitman in 1939 to compare regression
21 techniques when predicting the same validation set. This method compares the two sets of prediction
22 errors with a t-test to determine the significance of the difference. For the prediction of the validation
23 set of known variability (set 1), Foss Infratec 1241 and Bruins OmegAnalyzerG (s/n: 106118) were

1 significantly more precise within their brand ($\alpha = 0.05$). For the second validation set, results were
2 similar across instruments except for the prediction of oil where OmegAnalyzerG (s/n: 106110)
3 provided a better SEP than OmegAnalyzerG 106118 ($\alpha = 0.05$). In terms of fidelity, no clear pattern
4 could be observed. Because of their better precision and equivalent accuracies, Foss Infratec 1241 and
5 Bruins OmegAnalyzerG (s/n: 106118) were designated masters of their respective instrument brand
6 network.

7

8 *4.2 Intra-brand calibration transfer*

9

10 Figure 1 presents, for each parameter and brand network, validation results on both validation
11 sets. Performances of models developed on master units and transferred onto secondary unit are
12 compared with their respective master units. Dotted lines serve as reference for master results since
13 they were unchanged (and were omitted on the figure) by all orthogonal methods except O-PLS and
14 OSC.

15 Validation sets were different for protein ($\alpha = 0.05$; t-test for mean comparison) but not for oil.
16 The limited range for protein in validation set 2 was most likely responsible for these results along with
17 new variability brought in by 2006 crop year.

18 For protein, TOP and EROS gave significantly lower RPDs than other techniques for validation
19 set 1 (true for both brands) ($\alpha = 0.05$; t-test for mean comparison). The seven other methods did not
20 give different results. For the validation set 2, there was no difference. For oil and both validation sets,
21 there were also no significant differences ($\alpha = 0.05$; t-test for mean comparison). Even though results
22 were not significant, not all methods behaved the same way. Tables 4 and 5 summarize the
23 performance of the methods. Many of them gave better precisions than original models (table 4). A

1 couple of situations provided secondary units with better performances than the master unit (table 5).
2 This is an indication that removing the uninformative space representing the difference between
3 instruments can have a beneficial effect. This also shows that not all methods are appropriate for all
4 parameters and samples. A strong validation strategy must confirm the appropriateness of the method
5 to the situation of interest. It is interesting to notice that TOP 4years and EROS 4years did not perform
6 better than other methods even though they were designed to remove the variability through years.
7 Sequential and block DOPs performed well, especially for the Bruins network, while DOP did not do
8 well for that same network. The inclusion of more variability into the difference matrix helped to
9 remove the external information. Validation set 1 was less well predicted than validation set 2. This
10 could be explained by the fact that, since the validation set 1 and the calibration set are very close, too
11 much informative dimensions were removed, limiting the predictive ability of the model. However, the
12 model robustness was enhanced when predicting samples different from those in the calibration set.
13 This was particularly true for oil. This could mean that orthogonal methods tend to remove
14 informative information causing model to underfitting the data. This can be beneficial or a significant
15 constraint depending on the application.

16

17 In the present situation, TOP and EROS, as well as TOP 4years and EROS 4years respectively
18 gave the same results. Figure 2 presents the first four loadings of the D matrix between Infratec 1229
19 and Infratec 1241, after a PCA decomposition obtained from TOP (figure 2.a) and EROS (figure 2.b).
20 Both methods provided the same correction space. In TOP, the internal difference within classes (a
21 class being a sample collected on several instruments) is used to form a matrix whose variance is
22 analyzed while in EROS, the variance for each class is calculated, summed, and that sum is analyzed.

1 In situations where classes are the same, TOP and EROS provide the same results. TOP/EROS and
2 TOP/EROS 4years will be used from now and on to represent these methods.

3

4 *4.3 Inter-brand calibration transfer*

5

6 Figures 3 and 4 respectively present, for each parameter and validation set, the performances of
7 an Infratec model to be transferred onto Bruins units and vice-versa. For both situations (Infratec 1241
8 and OmegAnalyzerG 106118 master of the global network), and for both parameters, there is always a
9 method that will provide satisfactory calibration transfer results. The transfer of calibration models
10 across brands is possible and provides results as good as or better than if models were developed on
11 their own calibration sets.

12

13 For Foss Infratec 1241 master of the Bruins OmegAnalyzerG network, there were no significant
14 results for protein and validation set 1, but DOP, DOP 2y block, and OSC performed the best. For
15 validation set 2, only TOP/EROS provided as good results as the original model with all six other
16 methods significantly less precise ($\alpha = 0.05$). For oil and validation set 1, TOP/EROS, DOP 2y
17 sequential and DOP 2y block provided significantly lower RPDs than other methods while TOP/EROS
18 4years, and OSC provided OmegAnalyzerG 106118 with significantly higher results ($\alpha = 0.05$; t-test
19 for mean comparison). Finally, DOP 2y block performed again less precisely than other orthogonal
20 methods ($\alpha = 0.05$; t-test for mean comparison).

21

22 For Bruins OmegAnalyzerG 106118 master of the Foss Infratec network (Figure 4), there was
no significant difference for both parameters and validation sets. Depending on the situations, different

1 methods performed better than others, but this was not consistent from parameter to parameter and
2 validation set to validation set.

3

4 *4.4 Comparison with classical standardization methods*

5

6 Table 6 compares calibration transfer results from the best orthogonal methods for each
7 validation set, exhaustive calibration results, piecewise direct standardization, and slope and bias
8 correction, for intra-brand calibration transfer. The best performing orthogonal methods were found by
9 averaging results from both validation sets for the same parameter.

10 Secondary units performed globally better than when they were calibrated on their own
11 calibration set except for PDS that was proven to give significantly higher errors in Ref. [38]. Simple
12 methods performed as well as orthogonal methods. Exhaustive calibration models were overall the
13 best, but creating a calibration set including all variability is not always possible. The use of orthogonal
14 methods is a viable alternative for model transfer, in intra and inter-brand situations. For inter-brand
15 situations, similar trends were observed (data not shown).

16 The choice of transfer samples might be responsible for the present situation. While they were
17 chosen as being best predictors, which most likely influenced slope and bias results, they might not
18 have been completely appropriate for orthogonalization. Seeking standardization samples that optimize
19 orthogonal methods might be a better option.

20

21

22

23

1 *4.5 Evolution of the fidelity*

2
3 Improving or maintaining model precision is only part of the calibration transfer work. Keeping
4 the fidelity (mean difference between predicted and reference values) as good as on the master unit is
5 also challenging. In this study, intra-brand calibration transfer scenarios did not impact fidelity. Models
6 performed as accurately on the master unit as on the secondary units. However, in inter-brand
7 scenarios, orthogonal methods improved model fidelity which was not the case for exhaustive
8 calibration methods and slope and bias ones (data not shown). This may signify that a two-step
9 calibration transfer process may be needed: one to maintain precision and a second to correct for bias
10 loss.

11 12 *4.6 Orthogonal methods in calibration transfer*

13
14 The comparison of OSC, O-PLS, TOP/EROS, and DOP showed that performances were
15 instrument, parameter, and situation dependent. While OSC and O-PLS appeared more consistent, they
16 require the correction of validation samples, which is not always possible for on-line applications.
17 However, for off-line and compatible on-line applications, they remain two methods of choice for the
18 reduction of the uncorrelated part to \mathbf{Y} . DOP and TOP/EROS were proven to be two strong
19 competitors. For users willing to switch from classical methods (PDS, Slope and Bias) to orthogonal
20 methods, they are good candidates since they use standardization samples and are not as complex to
21 understand as OSC and O-PLS methods. They also have the advantage to not require the modification
22 of the validation samples. Their implementation will be possible on almost all instrument brands.

1 In the present study, DOP and its modifications appeared to perform better than TOP/EROS.
2 The creation of virtual standards was more suitable than scanning transfer samples on both units. The
3 noise generated with the virtual standards was most likely reduced and the orthogonal space removed
4 from \mathbf{X} was more representative of the inter-instrument differences. Virtual standards include
5 information from a lot more samples from the calibration set than only using standardization samples
6 that might poorly represent the variability encountered. Even-though more complex in its
7 implementation than TOP/EROS, DOP requirement for normality in the distribution of the reference
8 values can be stretched when tuning the kernel function. The possibility to combine the information of
9 several parameters to estimate \mathbf{D} provided an additional space for interference identification without
10 increasing the number of transfer samples scanned on the secondary unit.

11

12 **5. Conclusions**

13

14 This study compared the use of orthogonal methods with other common standardization
15 techniques for the transfer of calibration models between instrument of the same brand and across
16 brands. Orthogonal methods performed similarly to secondary units when calibrated on their own
17 calibration sets. While no method consistently outperformed others, no beneficial effect was observed
18 when using samples scanned at different periods of time to model instrumental variations (TOP/EROS
19 4years). Modifications to DOP provided good results and orthogonal methods using information in the
20 \mathbf{Y} matrix (O-PLS and OSC) performed better than most of other methods. O-PLS and OSC require
21 however the transformation of the validation samples and may not be suitable for all instrumental
22 setups.

1 The transfer of calibration models from brand to brand was possible, with an improvement of
2 initial model precision. A control of model fidelity must be performed to ensure proper predictions.
3 The two validation strategies demonstrated the necessity to evaluate the transferred models with future
4 variability.

5
6 **Acknowledgement**

7
8 Authors would like to acknowledge Pr. Tom Fearn for his help in implementing EROS and Dr.
9 Johan Trygg for his inputs on the O-PLS algorithm.

10

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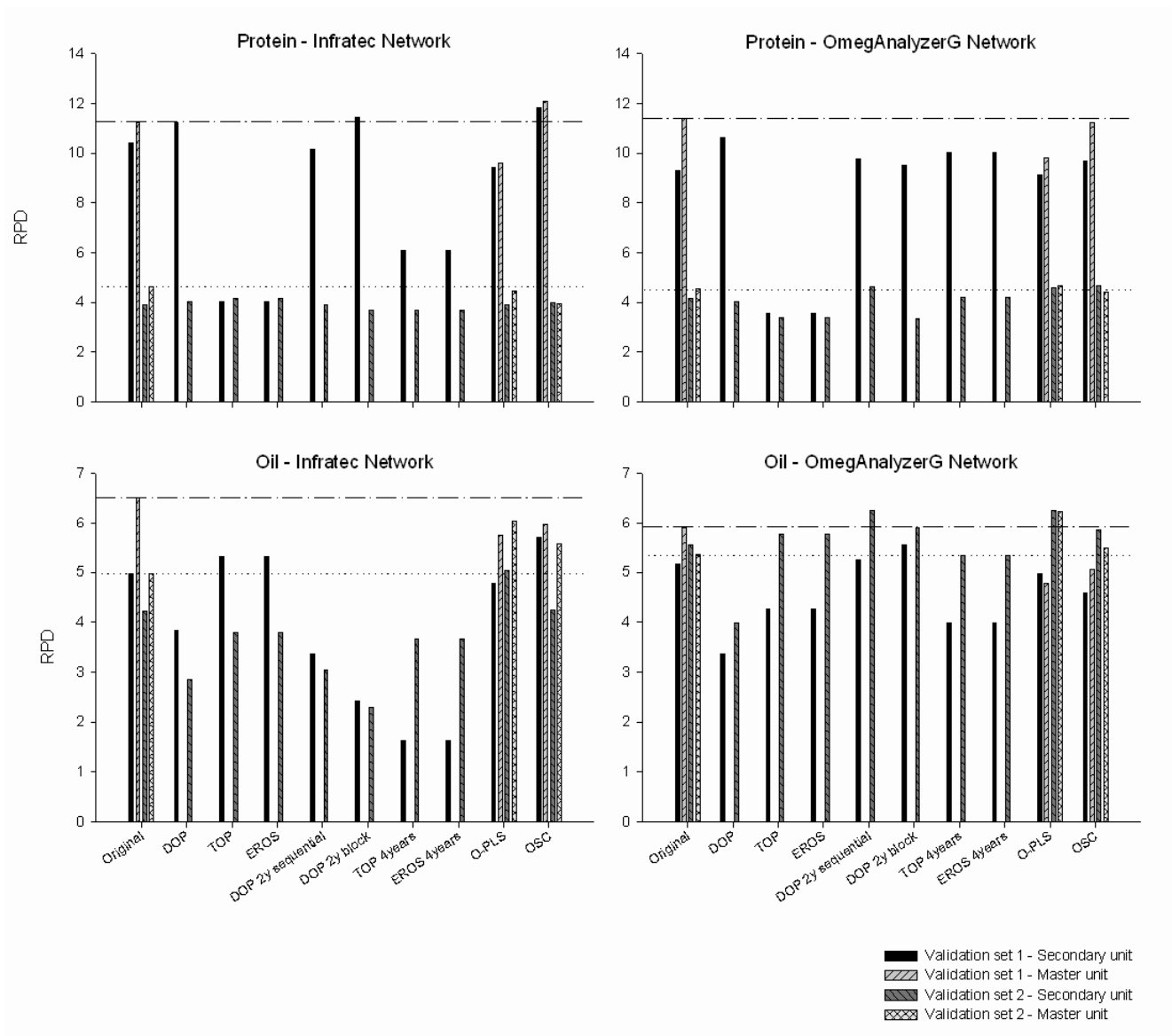
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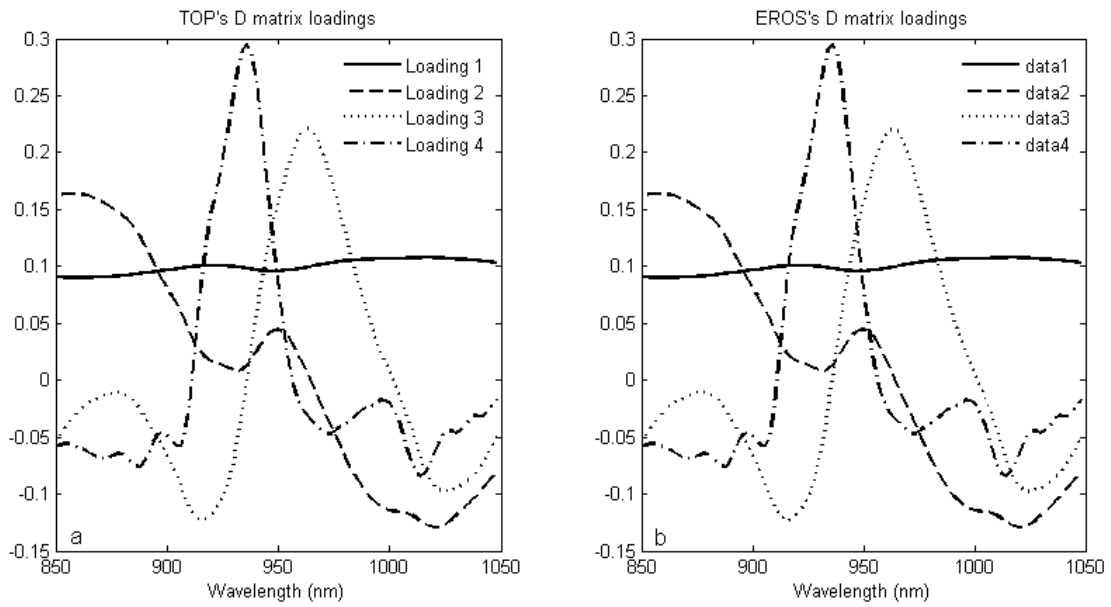


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2 Figure 1. Validation of the standardization methods in an intra-brand situation (Infracore 1241 is the
 3 master unit for Infracore 1229; OmegAnalyzerG (s/n: 106118) is the master unit for OmegAnalyzerG
 4 (s/n: 106110)). Dashed and dotted lines correspond to benchmark performances for validation set 1 and
 5 2 respectively.

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2 Figure 2. Loading vectors of the difference matrix D between Infratec 1229 and Infratec 1241 from a
 3 TOP decomposition (figure 2.a) and an EROS decomposition (figure 2.b).

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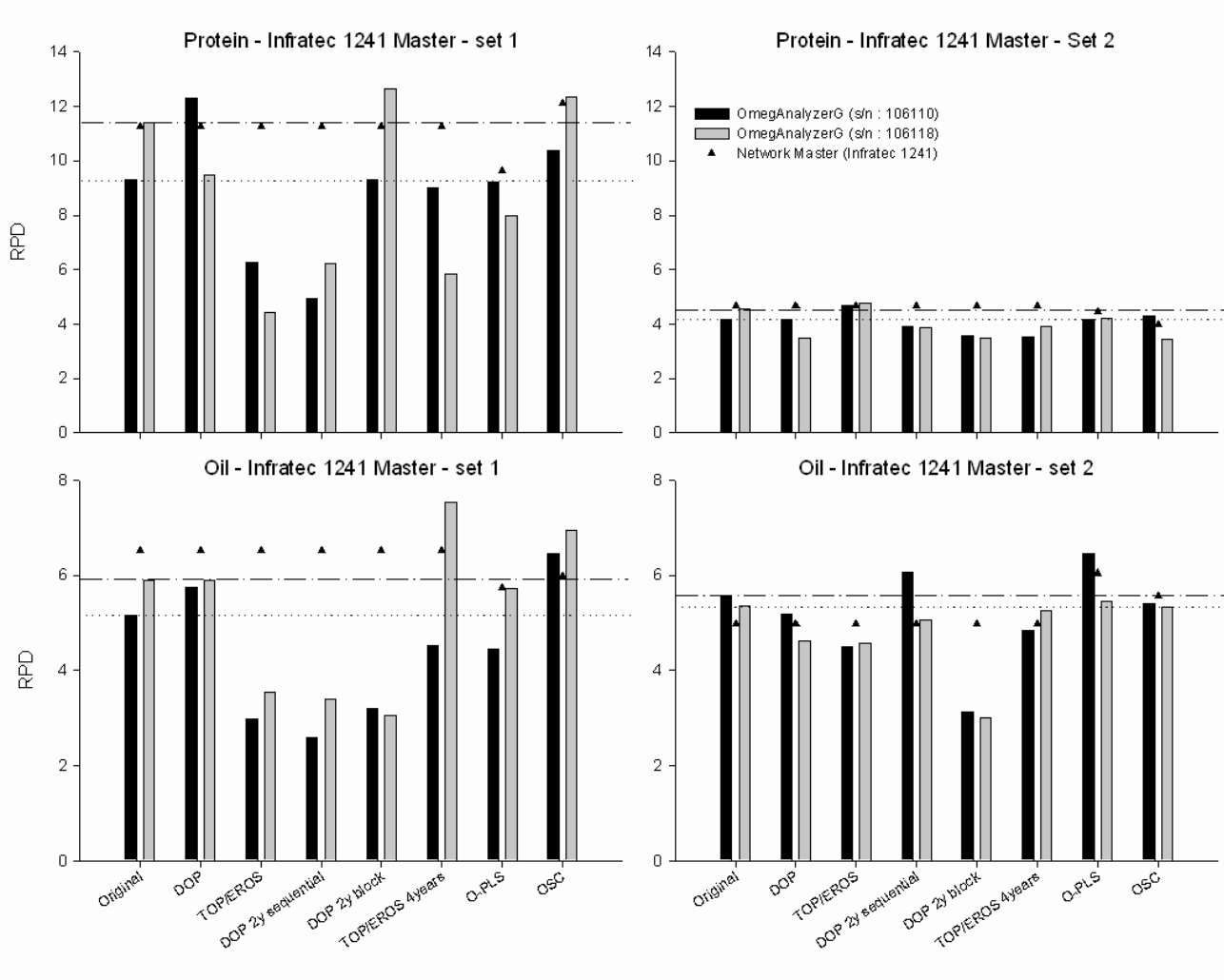
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2 Figure 3. Validation of the standardization methods in an inter-brand situation with Foss Infratec 1241
 3 master of the network. Bars represent secondary units while triangles are the performances of the
 4 master unit. Dotted lines correspond to benchmark results.

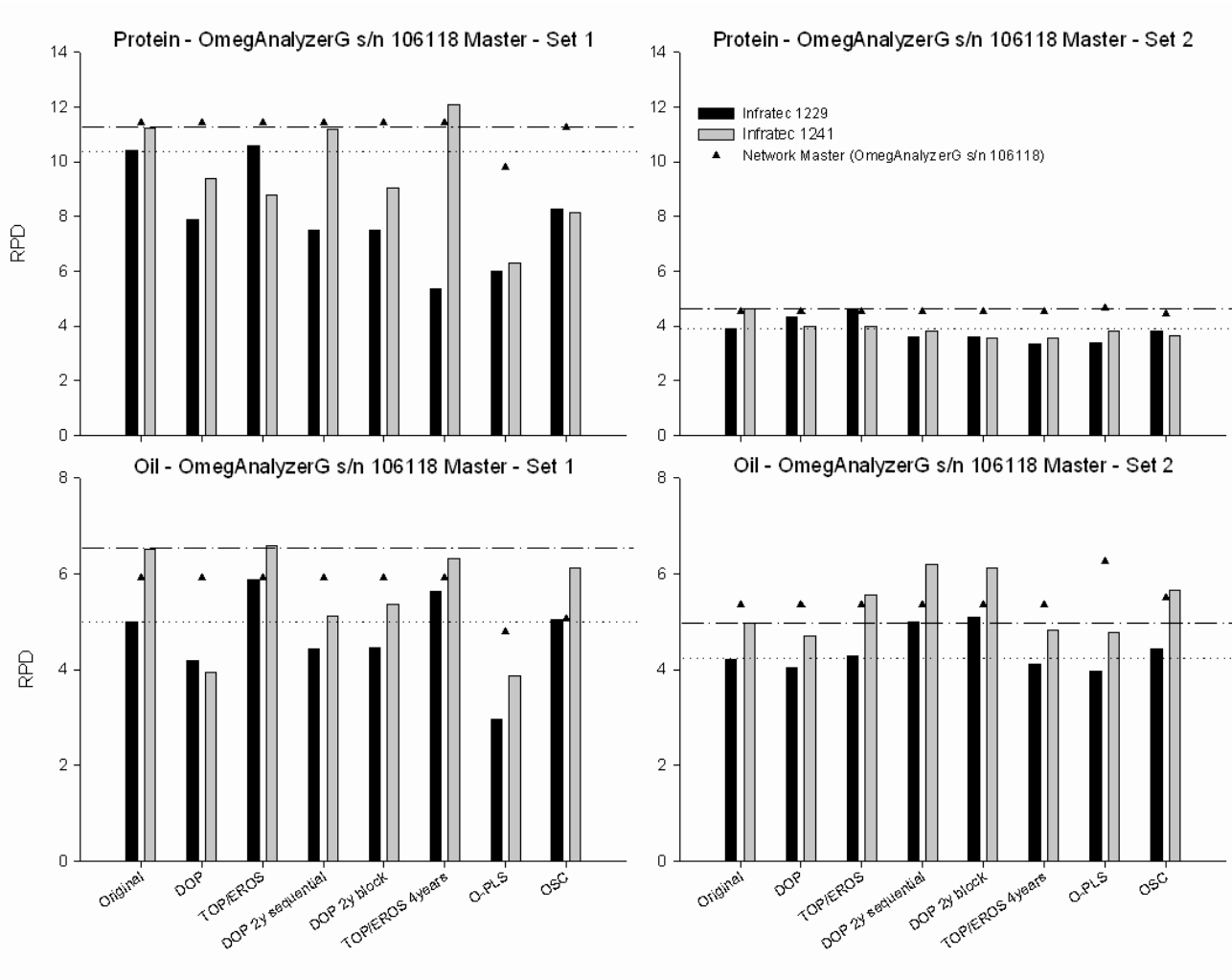
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2 Figure 4. Validation of the standardization methods in an inter-brand situation with Bruins

3 OmegAnalyzerG s/n 106118 master of the network. Bars represent secondary units while triangles are

4 the performances of the master unit. Dotted lines correspond to benchmark results.

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1 Table 1. Summary statistics of the calibration and validation sets.

2

Parameter	Instruments (serial)	n	Average Concentration (%)	Range (%)	Standard Deviation (%)
Protein (13% moisture basis)					
	Infratec 1229 (s/n: 553075)	638	36.06	29.74 - 46.50	2.80
	Infratec 1241 (s/n: 12410350)	624	36.04	29.74 - 46.50	2.76
	OmegAnalyzerG (s/n: 106110)	628	36.10	27.48 - 46.50	2.86
	OmegAnalyzerG (s/n: 106118)	625	36.09	27.48 - 46.50	2.92
	Validation set 1	20	36.72	30.65 - 45.43	3.32
	Validation set 2	40	37.61	33.78 - 41.92	2.14
Oil (13% moisture basis)					
	Infratec 1229 (s/n: 553075)	629	18.42	11.89 - 22.52	1.78
	Infratec 1241 (s/n: 12410350)	635	18.40	11.89 - 22.52	1.80
	OmegAnalyzerG (s/n: 106110)	655	18.51	11.89 - 22.52	1.73
	OmegAnalyzerG (s/n: 106118)	638	18.38	11.89 - 22.48	1.80
	Validation set 1	20	18.55	15.27 - 21.68	1.57
	Validation set 2	40	18.46	13.82 - 21.63	1.83

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1 Table 2. Summary of the different standardization used.

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Classical method	Orthogonal method on Y	Orthogonal method on X	Modified orthogonal method on X
PDS	OSC	TOP	TOP 4years
Slope and Bias	O-PLS	DOP	EROS 4 years
Exhaustive calibration		EROS	DOP 2y block
			DOP 2y sequential

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1 Table 3. Validation results of calibration models developed on their own calibration set.

2

Instruments (Serial)	Parameters	Validation set 1 (n = 20) (known variability)		Validation set 2 (n = 40) (unknown variability)	
		Protein	Oil	Protein	Oil
Infratec 1229 (s/n: 553075)	SEP ^{ac}	0.32	0.31	0.55	0.42
	RPD ^b	10.42	4.98	3.88	4.21
	Bias ^c	0.16	-0.14	0.12	-0.44
Infratec 1241 (s/n: 1241030)	SEP	0.30	0.24	0.46	0.36
	RPD	11.25	6.52	4.64	4.97
	Bias	0.20	-0.25	0.06	-0.40
OmegAnalyzerG (s/n: 106110)	SEP	0.36	0.30	0.51	0.32
	RPD	9.29	5.17	4.17	5.55
	Bias	0.12	-0.16	0.17	-0.48
OmegAnalyzeGr (s/n: 106118)	SEP	0.29	0.26	0.47	0.33
	RPD	11.41	5.90	4.54	5.35
	Bias	0.12	-0.23	0.16	-0.47

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4 ^a Standard error of prediction.

5 ^b Relative Predictive Determinant (unit less).

6 ^c SEP and bias are expressed in % pt.

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1 Table 4. Precision gain or loss provided by each standardization method compared to original
 2 calibrations.

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Method	Instrument	Protein		Oil		Number of latent variables		Number of component removed	
		Val. set 1	Val. Set 2	Val. set 1	Val. Set 2	Protein	Oil	Protein	Oil
DOP									
	Infratec 1229	+	+	-	-	10	12	1	1
	OmegAnalyzerG 106110	+	-	-	-	11	9	1	3
TOP									
	Infratec 1229	-*	+	+	-	12	11	1	1
	OmegAnalyzerG 106110	-*	-	-	+	12	11	1	1
EROS									
	Infratec 1229	-*	+	+	-	12	11	1	2
	OmegAnalyzerG 106110	-*	-	-	+	12	11	1	1
DOP 2y sequential									
	Infratec 1229	-	=	-	-	12	12	1	1
	OmegAnalyzerG 106110	+	+	+	+	12	12	1	1
DOP 2y block									
	Infratec 1229	+	-	-	-	11	12	1	1
	OmegAnalyzerG 106110	+	-	+	+	11	11	1	1
TOP 4years									
	Infratec 1229	-	-	-	-	9	10	2	3
	OmegAnalyzerG 106110	+	=	-	-	10	11	1	3
EROS 4years									
	Infratec 1229	-	-	-	-	9	10	2	3
	OmegAnalyzerG 106110	+	=	-	-	10	11	1	3
O-PLS									
	Infratec 1229	-	=	-	+	12	9	2	1
	OmegAnalyzerG 106110	-	+	-	+	12	8	2	3
OSC									
	Infratec 1229	+	+	+	=	10	9	1	1
	OmegAnalyzerG 106110	+	+	-	+	11	12	1	1

4

5 + result of the transferred secondary unit greater than the original secondary unit

6 - result of the transferred secondary unit lower than the original secondary unit

7 = results equivalent between transferred and original models

8 * marks significance

1 Table 5. Precision gain or loss provided by each standardization method compared to network masters.

2

Method	Instrument	Protein		Oil	
		Val. set 1	Val. Set 2	Val. set 1	Val. Set 2
DOP					
	Infratec 1229	=	-	-	-
	OmegAnalyzerG 106110	-	-	-	-
TOP					
	Infratec 1229	-	-	-	-
	OmegAnalyzerG 106110	-	-	-	+
EROS					
	Infratec 1229	-	-	-	-
	OmegAnalyzerG 106110	-	-	-	+
DOP 2y sequential					
	Infratec 1229	-	-	-	-
	OmegAnalyzerG 106110	-	+	-	+
DOP 2y block					
	Infratec 1229	+	-	-	-
	OmegAnalyzerG 106110	-	-	-	+
TOP 4years					
	Infratec 1229	-	-	-	-
	OmegAnalyzerG 106110	-	-	-	-
EROS 4years					
	Infratec 1229	-	-	-	-
	OmegAnalyzerG 106110	-	-	-	-
O-PLS					
	Infratec 1229	-	-	-	+
	OmegAnalyzerG 106110	-	=	-	+
OSC					
	Infratec 1229	-	-	-	-
	OmegAnalyzerG 106110	-	=	-	+

3

4 + result of the transferred secondary unit greater than the master unit

5 - result of the transferred secondary unit lower than the master unit

6 = results equivalent between transferred and master models

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1 Table 6. Transfer model performances with orthogonal and some common calibration transfer methods.

2

Instrument	Method	Protein (RPD ^c)		Oil (RPD)	
		Val. Set 1	Val. Set 2	Val. Set 1	Val. Set 2
Infratec 1229 – Master Infratec 1241					
	Original	10.42	3.89	4.98	4.22
	Best performing orthogonal (OSC ^a /OSC)	11.82	3.98	5.69	4.24
	Exhaustive calibration model	11.42	4.72	6.31	4.57
	PDS	5.51	3.25	6.92	5.02
	Slope and Bias	10.70	3.87	4.90	4.18
OmegAnalyzerG 106110 – Master OmegAnalyzerG 106118					
	Original	9.29	4.17	5.17	5.55
	Best performing orthogonal (DOP ^b /DOP 2y sequential)	10.62	4.01	5.25	6.26
	Exhaustive calibration model	11.39	4.44	5.48	5.73
	PDS	2.42	1.51	2.73	4.36
	Slope and Bias	9.59	4.16	5.34	5.67

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4 ^a Orthogonal Signal Correction.

5 ^b Dynamic Orthogonal Projection.

6 ^c Relative Predictive Determinant (unit less).

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