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Preliminary results of an interlaboratory study of chemometric software and methods on NIR data. Predicting the content of crude protein and water in forages ☆

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Abstract

Within the framework of the 'European Network for the Intercomparison of Chemometric Software and Methods,' a project supported by the European Commission, we have carried out a proficiency study on a near infrared spectroscopy (NIR) data set to determine how different the results from several laboratories were when they used their preferred multivariate calibration method and software. The data set was distributed to six participants, all of whom had previous knowledge and experience on multivariate calibration. The data consisted of NIR spectra of 305 forage samples recorded under the same conditions by a specialised laboratory. Two parameters were predicted, moisture at 103–105 °C and crude protein content. Results showed that the root mean square error of prediction (RMSEP) values obtained by all laboratories were acceptable, although they varied considerably. These results were preliminary and they will be used to properly define a final proficiency study in which more participants will collaborate.

Keywords: Interlaboratory data study; Chemometric intercomparison; Multivariate calibration; Forages intercomparison; NIR data intercomparison

1. Introduction

This paper presents a proficiency study for evaluating the differences in the results of six chemometric groups who applied different multivariate calibration methodologies in the analysis of the same data set. The Standards, Measurements and Testing (SMT) Pro-

☆ Discussion paper from the members of a chemometric working group.

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gramme of the European Commission is supporting a research project entitled European Network for the Intercomparison of Chemometric Software and Methods. This network is in fact an association of five national networks that are already devoted to apply research on chemometrics. These networks comprise more than 10 universities and some 25 companies. Unlike the well-known procedures for interlaboratory comparisons of chemical analysis methods [1], little has been done about interlaboratory chemometric methods comparison, even though from the industrial point of view, they are very much needed.

The main aim of the whole project, which takes the chemical approach as a reference, is the systematic and comparative study of chemometric methodology in various situations (similar to collaborative, proficiency and material certification studies) and with several types of data, including real data. These objectives, which are quite ambitious, have been distributed between all the national networks. Specifically, the goal of our local network was to produce and describe a near infrared spectroscopy (NIR) data set from which proficiency studies could be done in order to finally obtain a reference data set [2]. We will also develop protocols for carrying out a proficiency study and obtaining a reference data set.

The aim of this paper is therefore to present the results of a preliminary proficiency study carried out with a NIR forage data set. As all participating laboratories have used the same data set (as well as a unique test data set) and all have previous knowledge of multivariate analysis methods, there should be no significant differences. However, some disparities in the results have appeared.

Forages are natural products that are of vegetal origin. They may be transformed industrially into animal feed. They can be fresh or preserved, they may or may not contain additives and they are mostly organic, though they have some inorganic components. Forages are important because they are used in the production, transformation and consumption of agricultural products. According to EU legislation [3], farmers receive a subsidy for their dehydrated forages as long as the moisture of these forages is 12% or less and their crude protein is over 15%. These are the only conditions. Nowadays, near infrared spectroscopy (NIR) is widely used to analyse biological and agricultural samples without pretreatment [4–6] and specifically, diffuse reflectance is used to simultaneously analyse protein and moisture contents [7,8].

2. Participants

The participants were chemometric groups with previous experience using multivariate regression and calibration methods. They are listed in alphabetical order in Table 1. The Laboratori Agroalimentari de Cabrils (from the autonomous government of Catalonia, Spain), which is a specialised laboratory on agro-food feed analyses, recorded the NIR spectra and determined the reference values of the forage samples. Although the laboratory analysed the samples, they were not directly responsible for selecting the forage samples.

3. Experimental section

3.1. Samples

Three hundred and five different alfalfa forages (whole plants with stems, leaves, inflorescence) of different varieties (vegetative states, cuts, soils) were collected. They came from two different provinces of Catalonia (Barcelona and Girona) and were collected for over a period of 3 years (1996, 1997 and 1998) in the dehydrator industries, where they were submitted to the physical treatment of partial drying and gross grinding. Depending on the requirements of the clients that will buy those forages, samples were either pelletised or not. Representative samples of those processed in the dehydrator industries were sent to the laboratory,

Table 1
Participants in the proficiency study

- Departament de Química Analítica, Universitat Autònoma deo Barcelona, Spain
- Departament de Química Analítica, Universitat de Barcelona, Spain
- Departmentos de Química Analítica y de Matemáticas y Computación, Universidad de Burgos, Spain
- Departament de Química Analítica, Universitat Rovira i Virgili, Tarragona, Spain; coordinators of the local network
- Farmaceutische en Biomedische Analyse, Vrije Universiteit Brussels, Belgium
- Transformadora de Propileno, TDP, Tarragona, Spain

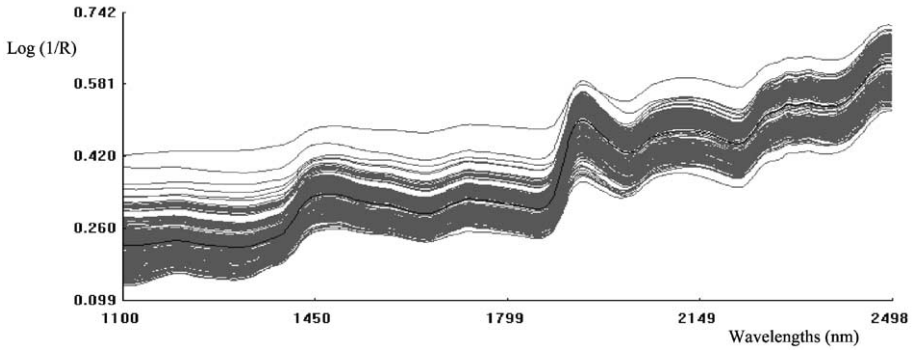

Fig. 1. NIR spectra recorded in the 1108–2492 nm range for the 305 forage samples.

where they were further submitted to new grinding to make them suitable for reference analysis, and their NIR spectra were measured. NIR spectra were recorded on a 6250 NIRSystems instrument.

3.2. Data characteristics

NIR reflectance spectra of the 305 samples were recorded in the 1108–2492 nm range (Fig. 1). The instrumental responses were taken every 8 nm, which means that there was a total of 174 wavelengths or variables. The reference values for moisture [9] were determined by leaving the samples in an oven at 103–105 °C for 4 h and weighed before and after the drying period. These values corresponded to the average of a triplicate analysis under repeatability conditions. Fig. 2 shows a distribution of the mean values for moisture. It can be seen that the moisture concentration range spanned from 3.12% to 14.51%. The mean value was 9.11% and the relative standard deviation was 1.34%. The content of crude protein was determined by the Kjeldhal method [10]. Fig. 3 shows a distribution of the mean values for the crude protein. These protein concentrations varied from 10.78% to 27.75%. The mean and standard deviation of protein values were 18.63% and 2.60%, respectively.

To calculate the intermediate precision of the reference values (SEL), some samples were selected from the 305 and reanalysed in intermediate precision conditions (that is, in different days) by duplicate. The SEL value was then calculated as the standard deviation of the differences between the analysis of these duplicates.

For moisture, 44 out of the 305 samples were considered and, as the selection was made at random, the moisture concentration range was between 5.17%

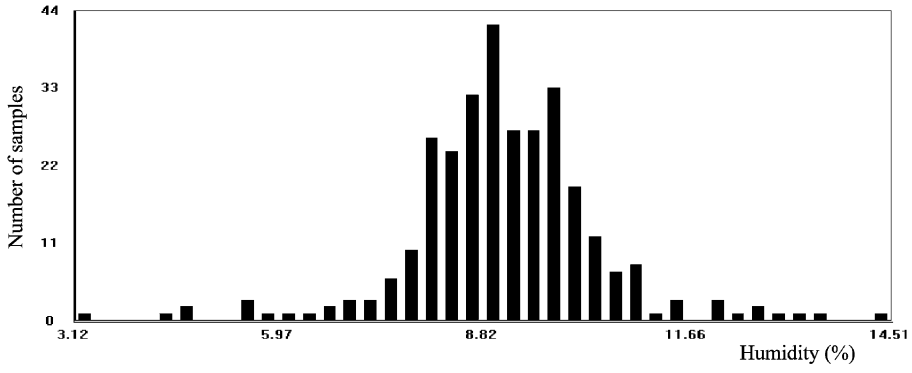

Fig. 2. Distribution of the forage samples according to the reference values for humidity at 103 °C.

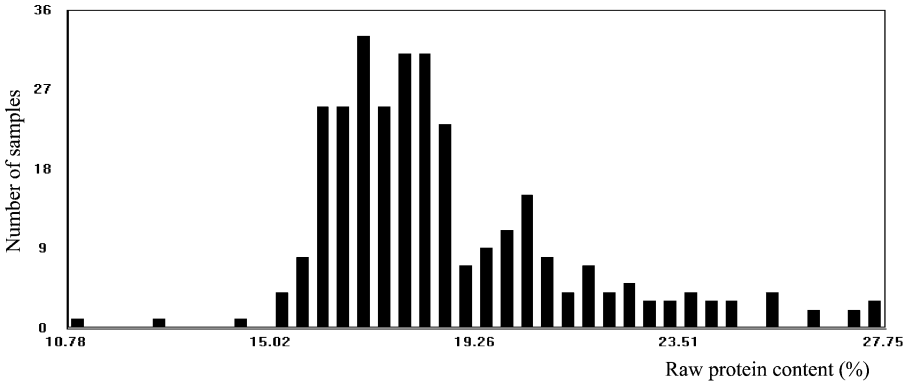

Fig. 3. Distribution of the forage samples according to the reference values for raw protein.

and 11.63% (weight/weight) being the moisture concentration average 9.14% (weight/weight). The SEL value was 0.24 which, when expressed as relative error, was %CV SEL = 2.6%. For crude protein, 91 different samples were considered out of the 305; the protein concentration range was between 13.41% and 25.0%, with the protein concentration average of 16.62%. In this case, for protein concentration, the SEL value was equal to 0.45 which, when expressed as relative error, was %CV SEL = 2.7%.

4. Organisation of the interlaboratory comparison exercise

There were no restrictions to carry out the multivariate data analysis, and all six participants selected their own specific parameters, such as the calibration method, the number of factors, the number and nature of calibration outliers, etc. However, in order to obtain comparable results among the six participating laboratories, the convenience of using a unique data set of samples to be used as a test prediction data set was agreed upon. Once the models were validated with this test prediction data set, the same mathematical expressions were used to report the results. The coordinators chose the test set from the 305 samples of forage by selecting an even number of samples, taking into account the range of the variables to be predicted. First, the data set was ordered from the minimum to the maximum according to the values of the variable to be predicted (moisture or protein concentrations). Then, one of every four samples was selected for the test set. The two data sets, one for each variable, were sent to all participants. The calibration set (for training and validating the model) contained 228 samples and the test set contained 77 samples.

All the participants were asked to supply the following information:

- Accuracy (RMSEP), bias, precision (SEP)
- Regression method and software used
- Pretreatments applied
- Strategy used for modelling
- Criteria for selecting the number of factors to build the model; number of factors
- Detection of outliers in calibration and test sets (criteria, number and sample identification)
- Individual predicted values for each sample of the test set
- Calibration line for predicted values against reference values (for the test set); slope, offset and correlation coefficient
- Residuals graph
- Any additional comments

All participants used the following mathematical expressions:

root mean square error of prediction :

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n}} \quad (1)$$

standard error of performance :

$$\text{SEP} = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i - \text{bias})^2}{n-1}} \quad (2)$$

$$\text{bias : Bias} = \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)}{n}. \quad (3)$$

5. General procedures

Within each laboratory, the internal procedure for building the models and predicting both moisture and crude protein content variables, was the same. These procedures are briefly described below.

5.1. Laboratory 1

Initially, the raw spectra were transformed into their second derivative by a Savitzky–Golay [11] algorithm with a second-order polynomial and a window size of 7 points. The 228 spectra available to build the model were analysed by PCA, while 85 samples were chosen to model moisture and 90 samples were chosen to model crude protein content, so as to encompass as much variability as possible in the plane described by the first and second principal components. The samples with maximum and minimum concentration values were also included in the calibration sets. PLS1 models (Unscrambler 7.5) were built for each of the predicted variables by cross-validation (using 10 randomly chosen segments). The significant number of factors was selected as the lowest that was not significantly different from the minimum MSECV (F-test, $\alpha = 0.25$). Regarding outliers in calibration, no outliers were detected for moisture and three samples (numbers 5, 7 and 65) were detected for raw protein. Regarding outliers in prediction, sample number 51 was detected for moisture and no outliers for raw protein.

5.2. Laboratory 2

After visual exploration of the data matrix, the raw spectra were transformed by the standard normal variate (SNV) technique [12]. The multivariate regression method used was PLS1 (Unscrambler 7.5), with 'internal evaluation set' as a validation method. Of the 228 samples given to build the calibration model, one out of four samples was selected for the internal evaluation set. Then, a calibration set of 172 samples and an internal evaluation set of 56 samples were obtained. The number of optimal factors was selected on the basis of Haaland's test and the Unscrambler's suggested number of factors. Regarding outliers for moisture, sample number 5 was detected in calibration and sample number 51 was detected in prediction. For the crude protein content, no outliers were detected either in calibration or in prediction.

5.3. Laboratory 3

The raw spectra were transformed into their second derivatives by the Savitsky–Golay [11] algorithm with a second-order polynomial to eliminate the scatter effect, decrease the overlapping of spectral bands and eliminate baseline changes. PLS1 (Unscrambler 7.5) was used as the multivariate regression technique. The significant number of factors was selected from cross-validation results of the calibration data set, looking for a minimum in the total validated residual Y-variance plot obtained for each component. Finally, outliers were detected on the basis of the plots of leverage, residual X-variance and residual Y-variance, as well as by principal component analysis and from the plots of the predicted values vs. the reference values. For both variables, five outliers (numbers 1, 3, 5, 6 and 8) were eliminated from the 228 samples of the calibration set. Three outliers in prediction were detected for moisture (numbers 1, 51 and 77) and two for raw protein (numbers 1 and 77).

5.4. Laboratory 4

After visual exploration of the data matrix, no pretreatment was applied to the raw data before the multivariate model was built. The multivariate regression method used was PLS1 (Unscrambler 6.1a), with cross-validation (leave-one-out) to select the significant number of factors from the plot of the total validated residual Y-variance obtained after each component. Before the final PLS1 model for predicting the moisture was obtained, five samples (numbers 1, 3, 6, 8 and 208) were removed because of their high leverage,

and two samples (numbers 5 and 10) were removed because their predicted values were far from their assigned concentration. To predict the crude protein content, the final PLS1 model was built without four samples (numbers 1, 7, 65 and 175) because of their high leverage value, one sample (number 171) because of its high residual and leverage value and four samples (numbers 6, 172, 215 and 219) because of their high residuals.

5.5. Laboratory 5

The raw spectra were transformed into their second derivative by a Savitzky–Golay [11] algorithm with a third-order polynomial and with a window size of 11 points. To obtain the regression model, internal cross-validation with three cancellation groups taken sequentially was used. The regression model was obtained by PLS1 (PLS Toolbox, Matlab version 2.01).

To select the number of latent variables, the laboratory: (a) determined the minimum RMSECV and removed the objects with a standardised residual above 2.5 (in absolute value), (b) repeated (a) until no further objects were removed or RMSECV dropped below 0.24 and (c) used bootstrap (resampling size 10 000) on the distribution of the residuals of the calibration samples to find the number of latent variables that give the same value for RMSEC at 95%.

To determine RMSEP, SEP and bias, the following was accomplished. (a) The laboratory determined whether the spectrum of each sample was analogous to those of the calibration. To do this, the leverage of the samples on the space of latent variables was calculated. If the leverage was high, i.e., the T^2 statistic was higher than the critical value at 95%, the sample was removed. (b) The laboratory used a robust method to find the central value and a dispersion parameter (a kind of robust estimate of the standard deviation) of the distribution of residuals. To avoid new notation, these robust estimators will be called Bias and SEP, respectively. The square of RMSEP is then calculated by summing the squares of both estimators.

Outliers were detected, both in calibration and in prediction. For moisture calibration, five samples

Table 2
Results for moisture at 103 °C obtained by each participant with the forages data set

Parameters	Laboratories					
	1	2	3	4	5	6
Regression method	PLS	PLS1	PLS1	PLS1	PLS1	PLS1
Program	Unscrambler 7.5	Unscrambler 7.6	Unscrambler 7.5	Unscrambler 6.1a	Matlab 2.01 PLS Toolbox	Matlab 5.2
Pretreatment	second derivative Savitzky–Golay	SNV	second derivative Savitzky–Golay		second derivative	
Calibration	PCA, maximum and minimum	one sample out of four	cross-validation	cross-validation	cross-validation, three cancellation groups	cross-validation, leave-one-out
Number of calibration samples	85 modelling	171 modelling, 56 test	223	221	223	227
Outliers in calibration	0	1	5	7	5	1
Number of validation samples	76	76	74	72	71	75
Outliers in prediction	1	1	3	5	6	2
Factors selection	minimum MSCEV (F-test)	minimum MSCEV (F-test)	minimum PRESS vs. number of factors	Y-variance vs. number of factors	minimum RMSECV bootstrap	RMSCV vs. number of factors
Number of factors	7	6	3	3	9	3
RMSEP	0.268	0.221	0.2835	0.274	0.207	0.322
SEP	0.267	0.223	0.2818	0.275	0.207	0.384
Bias	−0.036	−0.006	−0.045	−0.023	0.007	−0.03
Slope	1.03	0.97	1.01	1.1	1.1	1.06
Offset	−0.38	0.2	−0.27	−0.74	−0.66	−0.67
Correlation	0.896	0.904	0.932	0.924	0.897	0.891

(numbers 1, 5, 8, 116 and 180) were detected as outliers. For crude protein content calibration, five samples (numbers 1, 98, 162, 201 and 219) were detected as outliers. For moisture prediction, six samples (numbers 1, 2, 21, 51, 71 and 77) were detected as outliers, and for crude protein content prediction, nine samples (numbers 1, 4, 12, 15, 17, 30, 47, 58 and 64) were detected as outliers.

5.6. Laboratory 6

No pretreatment was applied to the NIR data. A PLS1 (PLS Toolbox Matlab version 5.2) regression model was built by cross-validation and leave-one-out cross-validation was used to compute RMSCV values to assess the model performance. The optimal model was considered to be the one with the number of PLS factors for which the RMSCV was minimum when the RMSCV values were plotted against the number of PLS factors. Both in calibration and in prediction, outliers were detected. One sample (number 5) was detected for the moisture model as a calibration outlier, but no outliers were detected for the calibration of crude protein. Several methods were used to detect outliers in prediction. Methods based on the study of residuals, such as calculating the root mean square error in spectral residuals (RMSSR) or calculating the total residual standard deviation (TRSD), detected two samples (numbers 1 and 51) as prediction outliers for moisture, but no outlier was detected for crude protein.

6. Results

Tables 2 and 3 summarise the procedures followed by each participant for predicting moisture and protein, respectively, and the results they obtained. A number has been assigned to each laboratory to maintain anonymity. Fig. 4 shows the regression lines (predicted moisture vs. reference values) for the 77 objects of the test set for the six laboratories. Fig. 5 shows the residuals obtained by these calibration lines. Similarly, Figs. 6 and 7 show the regression lines and the residuals for the prediction of the crude protein content

Table 3
Results for raw protein content obtained by each participant with the forages data set

Parameters	Laboratories					
	1	2	3	4	5	6
Regression method	PLS1	PLS1	PLS1	PLS1	PLS1	PLS1
Program	Unscrambler 7.5	Unscrambler 7.5	Unscrambler 7.5	Unscrambler 6.1a	Matlab 2.01 PLS Toolbox	Matlab 5.2
Pretreatment	second derivative Savitsky–Golay	SNV	second derivative Savitsky–Golay		second derivative	
Calibration	PCA, maximum and minimum, cross-validation	one sample out of four	cross-validation	cross-validation	cross-validation three cancellation groups	cross-validation, leave-one-out
Number of calibration samples	90 modelling	171 modelling, 57 test	223	219	223	228
Outliers in calibration	3	0	5	9	5	0
Number of validation samples	77	77	75	71	68	77
Outliers in prediction	0	0	2	6	9	0
Factors selection	minimum MSCEV (F-test)	minimum MSCEV (F-test)	minimum PRESS number of factors	Y-variance vs. number of factors	minimum RMSECV bootstrap	RMSCV vs. number of factors
Number of factors	8	7	8	6	9	8
RMSEP	0.912	0.956	0.8271	0.781	0.668	0.939
SEP	0.903	1.954	0.8263	0.787	0.666	0.764
Bias	−0.166	0.016	−0.101	−0.008	−0.049	9.7 e−14
Slope	0.93	0.81	0.90	0.80	0.88	0.82
Offset	1.09	3.33	1.73	3.51	2.10	3.29
Correlation	0.947	0.942	0.9523	0.925	0.959	0.945

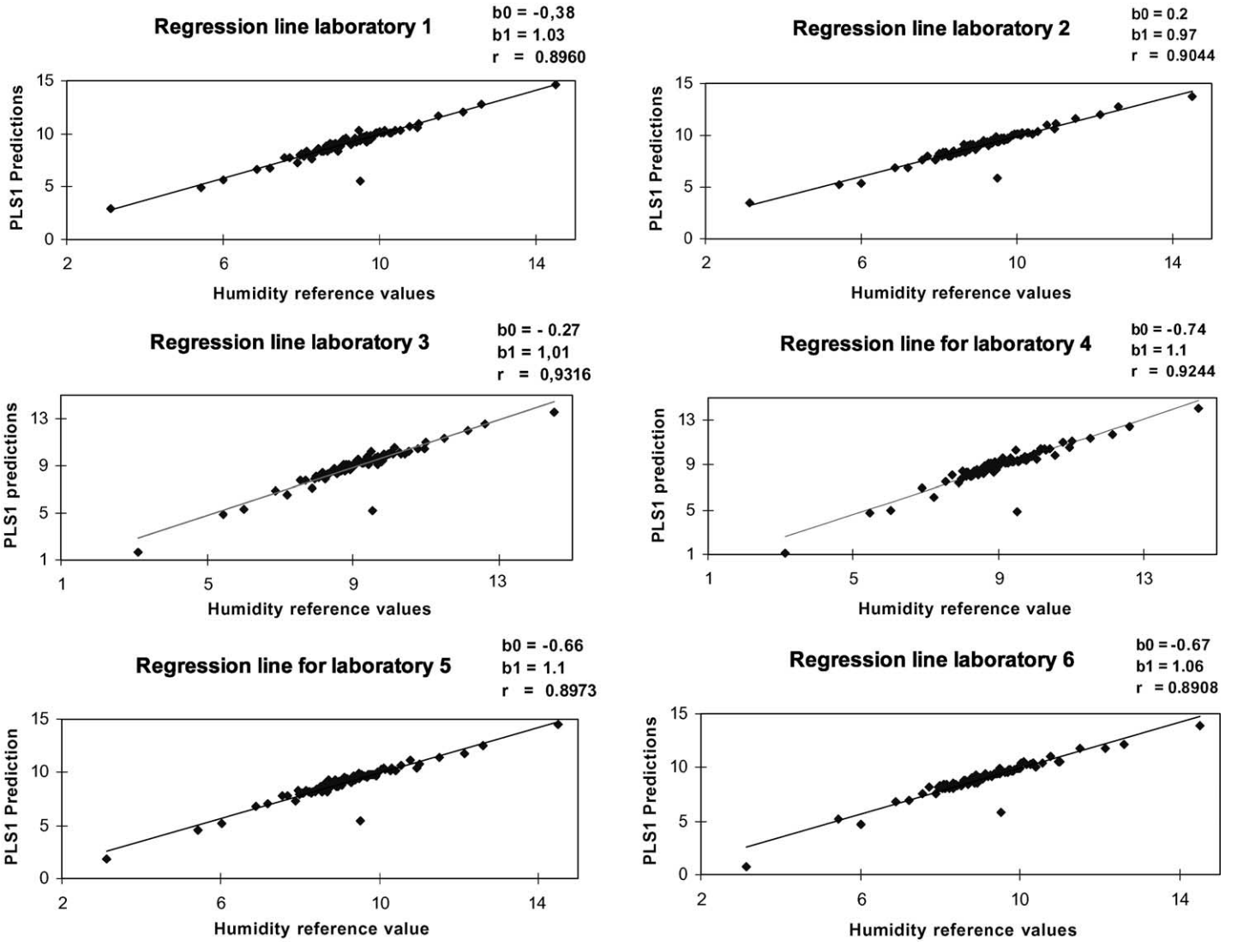

Fig. 4. Regression line for predicted humidity vs. reference values for the 77 objects of the validation set by all six participants.

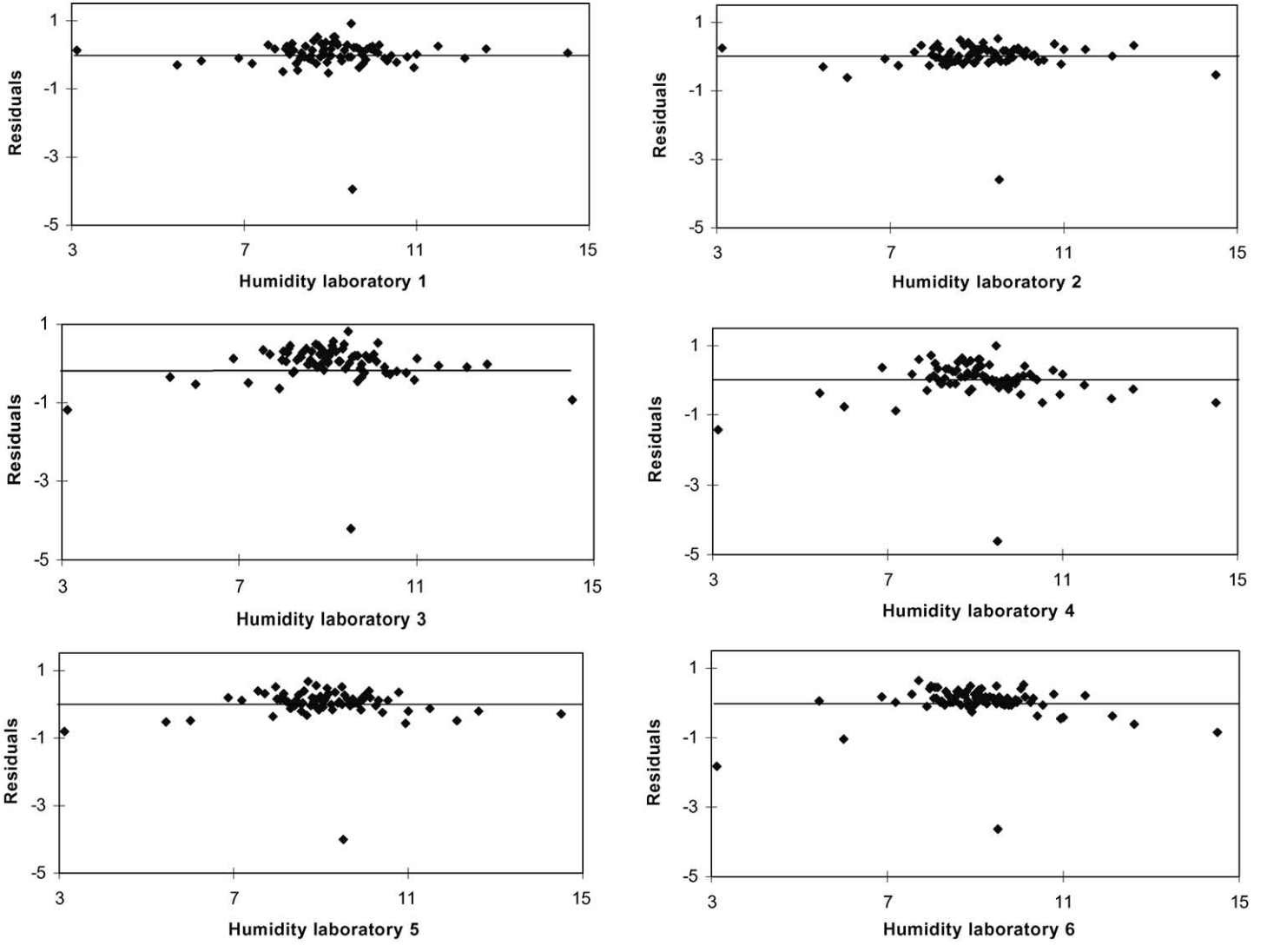

Fig. 5. Residuals corresponding to the calibration line in Fig. 4 obtained by all six participants.

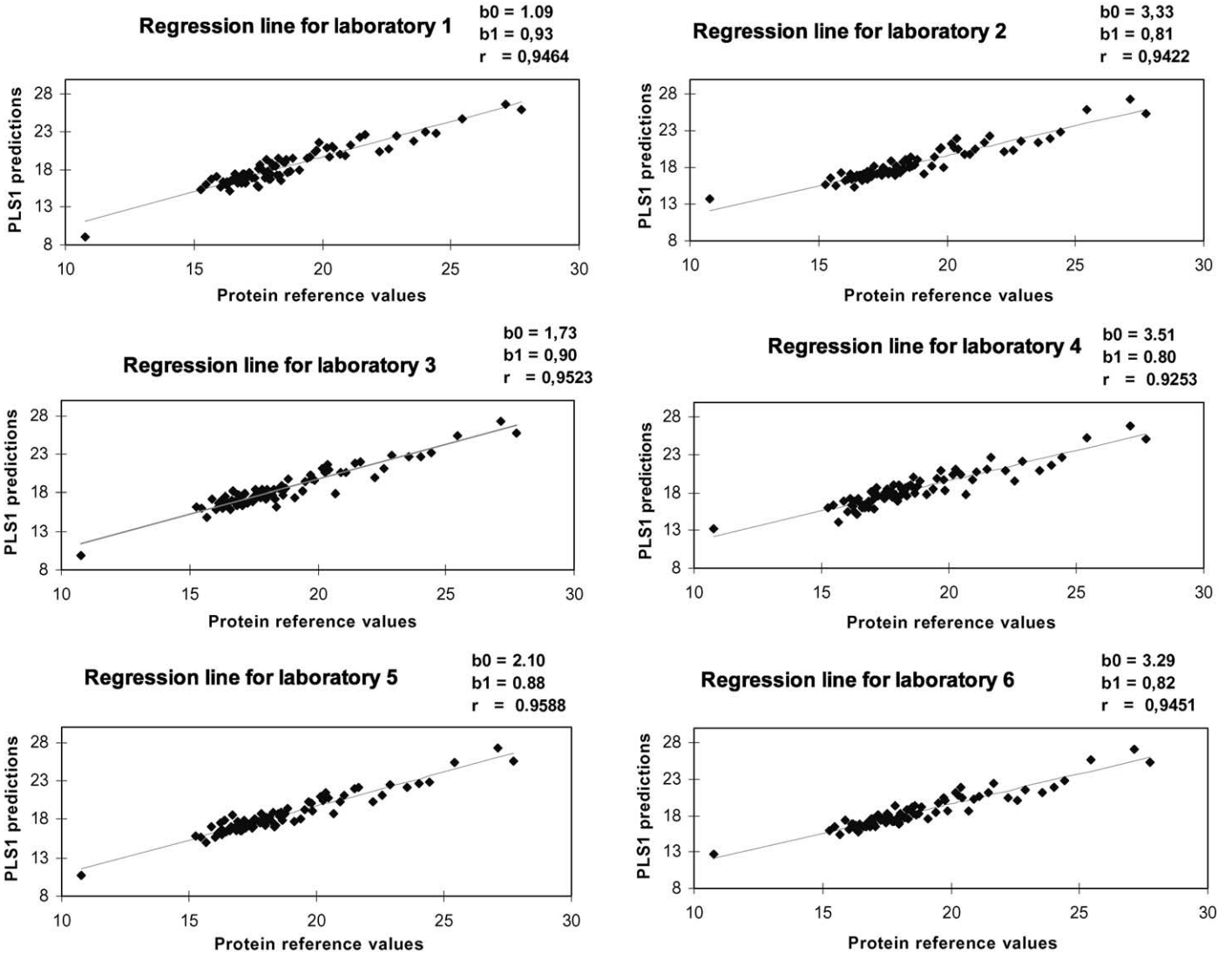

Fig. 6. Regression line for predicted raw protein vs. reference values for the 77 objects of the validation set by all six participants.

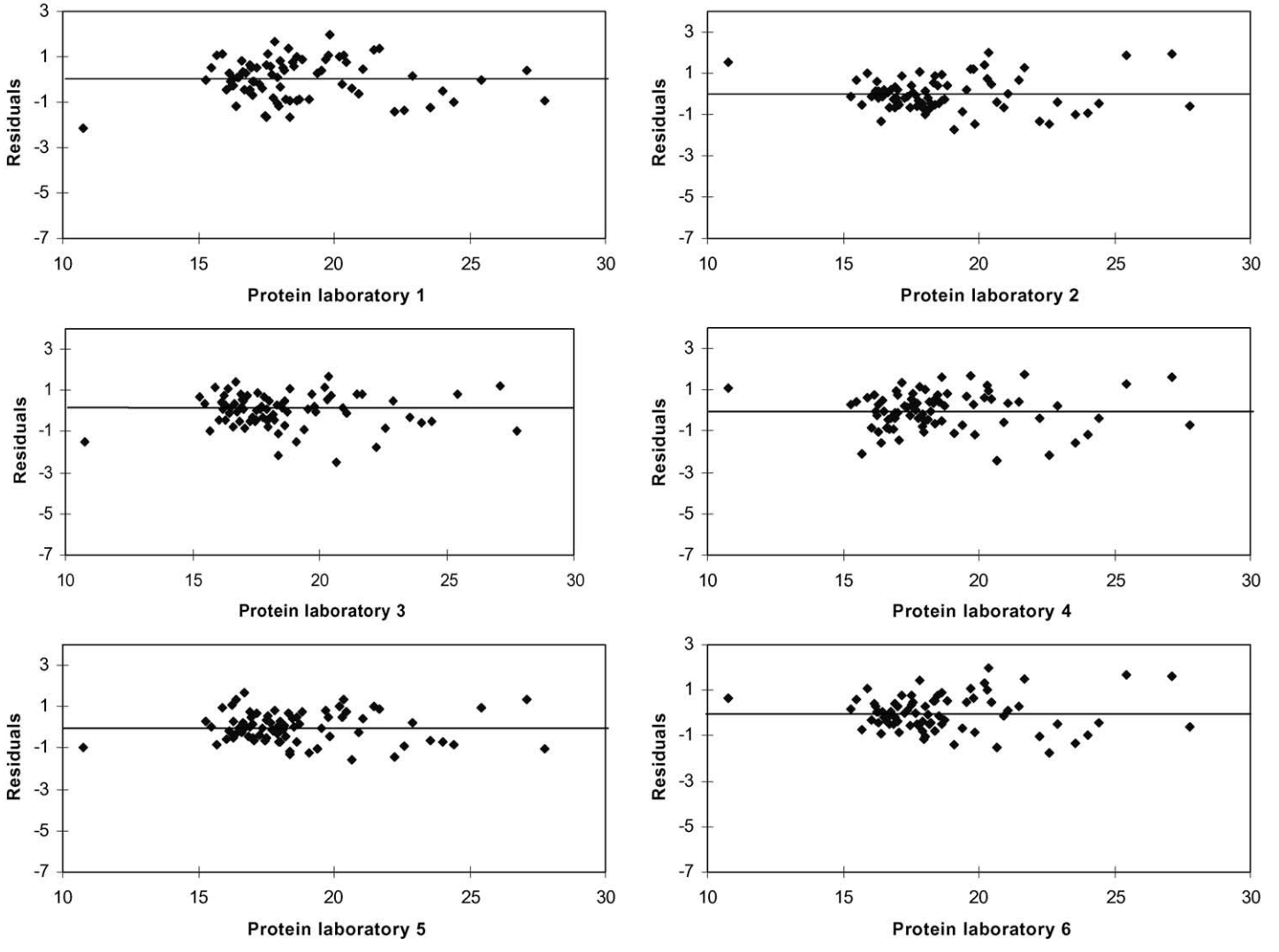

Fig. 7. Residuals corresponding to the calibration line in Fig. 6 obtained by all six participants.

for the 77 objects of the test set. All parameters regarding the calibration lines and residuals correspond to the 77 objects of the test set, not considering outliers in prediction. The rest of statistical parameters specified in Tables 2 and 3 have been calculated considering the outliers detected by each partner.

All participants used the same regression method (PLS1), but their software were different: altogether, two versions of Unscrambler (7.5 and 6.1) and two versions of the PLS Matlab Toolbox (2.0 and 5.2) were used. Nearly all the laboratories applied a different pretreatment. The most used ones were second derivatives using Savitzky–Golay [11] with different polynomial order and different window widths and standard normal variate (SNV) [12].

Most participants used cross-validation to build and evaluate the calibration model. However, two participants used an internal test set to validate the model, so the calibration set was divided into two data sets. One participant selected the calibration samples from the PCA plot and the samples with the maximum and minimum values for the variable to be predicted. Another participant selected the calibration set by taking one object out of four from the initial calibration set (228 samples).

Participants also had some different criteria for selecting factors. Some of the participants selected the number of factors giving a minimum on the plot of RMSCV or PRESS values vs. the number of factors. Also, Haaland's *F*-test was used, as well as other not-so-common procedures.

Results for moisture at 103–105 °C showed that the different criteria chosen for selecting the number of factors gave different models (from three to nine factors). The number and type of outliers detected in the calibration and prediction steps were also quite different. All participants except one (laboratory 1) detected outliers in the calibration step; two participants detected five outliers and another one detected seven outliers. Sample number 5 was always detected as an outlier. In the prediction step, there was also a lot of diversity in this respect; for example, two laboratories detected one outlier and one laboratory detected as much as six outliers. All participants detected sample number 51 as a ubiquitous outlier. In general, RMSEP values were in agreement, ranging from 0.207 to 0.322. Finally, no participating laboratory detected any considerable bias in the models. These values ranged from -0.006 to -0.131, which were considered rather low.

Since the discussion of the results for the protein content would be similar to those for moisture, we will only discuss the more significant differences. Prediction of the crude protein content gave rise to bias detection in one case. Also, RMSEP values for crude protein were higher than for moisture. The number and the specific outliers detected in both calibration and prediction were very diverse.

7. Conclusions

For a reliable comparison of the results of the proficiency study, it should be considered that all participants did work with the same test data set. However, our results showed that the internal methodology used by each participant was different. The only parameter that was the same for all participants was the regression method (PLS1), but even in this case, they were using different software packages. The RMSEP values obtained by each laboratory were rather low, but they showed some variations, which were unforeseen since, as we have already mentioned, they refer to the same test data set and all the participants have considerable experience in working with multivariate data analysis. Tables 2 and 3 showed that the RMSEP values for crude protein were worse than those for moisture. This is reasonable because the sample distribution according to moisture and protein content (Figs. 2 and 3) showed that the values for crude protein were very diverse.

As it has been stated, there was a high diversity in the number of samples detected as outliers, either in the calibration or in the prediction steps. Not only were the total number of outliers different, but the samples selected as outliers were also different. Only two outliers were the same for all laboratories: number 5 for moisture calibration and number 51 for moisture prediction. For raw protein, the detected outliers were always different. This situation requires a deeper study on the criteria followed for outliers detection. This study is being done at present by other areas of the network.

A comparison of the SEL and SEP values shows reasonable agreement between them. The SEP values for moisture varied from 0.207 to 0.322, while the SEL

value was 0.24. It can be stressed that the laboratory with the lowest SEP value was the one that used a higher number of factors (up to nine), had a higher slope of the straight line obtained in the predicted vs. reference values and was the one who eliminated the highest number of outliers (five in calibration and six in prediction). This might be an indication of an overfitted model. In a similar way, for raw protein, SEP values varied from 0.668 to 0.956, while the SEL value was 0.45.

These have been preliminary results that were useful to define the protocol for a final proficiency study with a greater number of participants. After this final study, a new protocol for a proficiency study to compare interlaboratory chemometric methods and generate a reference data set with real data will be developed. This new reference data set will be useful for assessing, for example, the suitability of new laboratory-made software.

Last but not least, the information sent to the laboratories and the information each laboratory reports back should be clearly specified and coordinated in order to avoid misunderstanding and misinterpretation. This is due to the many variations that are possible in chemometrical analysis.

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