Quality control system in a routine laboratory using near infrared spectroscopy

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Introduction

The crop laboratory of Blgg analyse about 100,000 forage samples a year. In most samples the feeding value has to be determinated. To analyse the constituents needed to calculate the feeding value near infrared spectroscopy (NIR) is used. To maximise sample throughput and standardise sample presentation to the NIR instrument, Blgg has automated sample input.[1] With this instrumentation it is possible to analyse up to 100 dried and ground samples an hour. The constituents predicted using NIR for different products are given in Table 1.

Table 1. Predefined prediction errors ($RMSEP_{goal}$) for the different product and constituents used at Blgg.

Product constituent	Corn silage	Grass silage	Grass fresh	Cereal silage
moisure (g· kg^{-1})	3.6	—	3.6	—
crude ash (g· kg^{-1} DM)	3.5	8.0	8.0	8.0
crude protein (g· kg^{-1} DM)	4.0	9.0	8.0	8.0
crude fibre (g· kg^{-1} DM)	9.0	10.0	9.0	10.0
NDF[1] (g· kg^{-1} DM)	15.0	15.0	—	—
ADF[2] (g· kg^{-1} DM)	10.0	10.0	—	—
ADL[3] (g· kg^{-1} DM)	7.5	7.5	—	—
sugar (g· kg^{-1} DM)	10.0	10.0	10.0	10.0
starch (g· kg^{-1} DM)	15.0	—	—	15.0
OMD[4] (%)	0.9	1.6	1.4	1.6

NDF[1] = neutral detergent fibre
ADF[2] = acid detergent fibre
ADL[3] = acid detergent lignin
OMD[4] = organic matter digestibility

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To control the quality of the large amount of data coming from this system, a quality control system has been developed. The system is derived from the quality control system used at the laboratory for the other analytical methods.
The system consists of three parts:

- daily instrument control, to check the instrument every morning on its specifications and stability
- first line control, to check the quality of the produced data
- moving validation, to control the whole system, from sample preparation to final results.

Material

Daily instrument control

The NIR analysis are performed using a NIRystems 5000 (Foss) connected to an autosampler (Kiestra Instrumentmakers). Every morning, one hour before the operator arrives the instrument is switched on using a timer and a batchjob. After the instrument is warmed up the specifications are recorded using the diagnostics module of ISI-software driven by a macro. The bias, noise, wavelength error, instrument response and dark period value, are stored in an ASCII-file. Next, a sealed check cell filled with a corn silage sample is analysed. The calibrations used to analyse the check cell are derived from the combined forage product databases. The results of the constituents (moisture, crude ash, organic matter digestibility, crude protein, crude fibre, sugar and starch) and the Global and the Neighbourhood *H*-values are stored in an ASCII-file together with the data of the diagnostics (see Table 1).

To judge whether these data are in control, Shewhart charts[2] are used. The nominal values of the constituents are fixed at the historical average values. The control limits are set at the instrument specifications, when available. For the constituents of the check cell the control limits are set at three times the historical standard deviation of the particular constituent. Execution of instrument control only takes ten minutes of operator time, but provides a lot of valuable data on the performance of the instrument.

First line control

A first line control is a common procedure in an analytical laboratory.[3] In every batch of samples to be analysed one or more quality check samples are analysed too. The material of the quality check sample is comparable with other samples in the batch. When the analysis of a batch of samples is completed the results of the quality check samples are plotted in a Shewhart chart. In these Shewhart charts the nominal value is fixed at the historical average value of the constituent. The control limits are based on the prediction error the constituent has to meet ($RMSEP_{goal}$). The control limits are calculated as $3 \times 0.5 \times RMSEP_{goal}$. The $RMSEP_{goal}$ values are specified for each constituent and product (see Table 1).

Moving validation

For the moving validation samples analysed using NIR are selected using a fixed interval on order of entrance. Next to the NIR analysis, the selected samples are analysed again by using the reference methods. For every constituent the differences between the results of the NIR and the reference-methods are put in Shewhart charts. In these charts the nominal value is, of course, zero. The control limits are set at $\pm 3 \times RMSEP_{goal}$.

Out of control of the process is defined as 1 time outside a control limit or 2 out of 3 consecutive times outside 2/3 of a control limit. When the process is out of control the results are plotted as boxes in

Table 2. Data table containing the daily instrument control data.

Date	Instrument noise		Wavelength accuracy			Instrument response		→» Results of sealed check cell								
									Crude		Crude		Crude			
	bias	RMSc	Error	Kappa	Phi	Max. R	Dark P	Moisture	Ash	OMD	Protein	Fibre	Sugar	Starch	G–H	N–H
..-..-1998																
..-..-1999																
11-05-99	–5	9	0.1912	3312.42	0.31745	57998	840	59.62	48.08	75.28	79.23	197.65	19.54	337.58	0.67	0.44
11-05-99	–5	9	0.1912	3312.42	0.31745	57998	840	57.39	45.77	75.59	77.45	197. 91	20.36	343.28	0.69	0.37
12-05-99	–6	10	0.1973	3312.40	0.31746	58353	844	58.13	47.72	75.69	77.14	197.83	20.45	341.23	0.70	0.39
12-05-99	–6	10	0.1973	3312.40	0.31746	58353	844	58.13	47.72	75.69	77.14	197.83	20.45	341.23	0.70	0.39
14-05-99	–2	9	0.1992	3312.40	0.31747	58526	848	58.09	49.20	75.56	76.64	200.07	18.09	339.71	0.67	0.37
17-05-99	–1	11	0.2314	3312.34	0.31751	58222	848	61.42	43.81	75.29	80.52	197.71	22.79	337.11	0.71	0.39
18-05-99	–8	8	0.2326	3312.30	0.31751	58421	849	63.97	48.28	75.84	79.09	203.88	18.75	334.05	0.67	0.38
19-05-99	–5	9	0.2101	3312.31	0.31750	58420	849	63.42	49.25	75.50	77.90	203.41	20.25	334.20	0.66	0.37
20-05-99	+0	12	0.2186	3312.30	0.31750	58665	849	61.77	50.82	75.29	79.01	203.62	20.28	335.22	0.70	0.39
21-05-99	–4	0	0.2247	3312.29	0.31751	58733	849	62.03	48.99	75.43	77.17	204.01	20.67	333.93	0.72	0.35
25-05-99	–3	12	0.2392	3312.32	0.31751	58503	849	63.14	48.16	75.42	76.92	204.27	18.80	336.64	0.76	0.36
26-05-99	–4	8	0.2312	3312.30	0.31752	58610	851	62.72	48.78	75.81	76.22	203.82	18.48	334.82	0.78	0.37
27-05-99	–7	9	0.2413	3312.30	0.31752	58570	851	62.46	50.46	75.26	76.62	205.11	17.47	339.21	0.76	0.38
28-05-99	–7	14	0.2206	3312.28	0.31751	58562	852	62.58	50.22	75.70	78.34	202.99	19.03	337.76	0.72	0.38
31-05-99	–4	11	0.2400	3312.29	0.31752	58349	854	61.99	49.83	75.64	74.53	204.64	15.63	339.62	0.74	0.35
01-06-99	–9	10	0.2353	3312.30	0.31751	58311	857	62.14	51.43	76.20	78.28	202.75	21.24	337.39	0.72	0.35
02-06-99	–5	11	0.2263	3312.29	0.31751	58228	856	56.21	48.93	75.97	74.61	199.18	13.16	344.36	0.62	0.27

OMD* = Organic Matter Digestibility
G–H* = Global H value
N–H* = Neighborhood H value

stead of plus signs. When a response value is out of control action has to be taken to get the process in control again. Changes in the process (drift in average or variance) can be detected even when the process is in control.

Results

Daily instrument control.

In Table 2, a part of the table containing the daily instrument control data is shown. For each constituent from this table a Shewhart chart is plotted. In Figure 1 the Shewhart chart of the instrument noise is shown. The upper control limit is set at 20 micro log, according the instrument specifications.

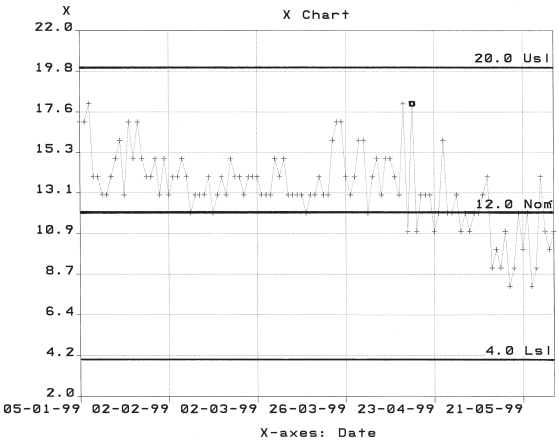

Figure 1. Daily instrumental control. Y-axes: instrument noise as *RMS*(*c*) (micro log).

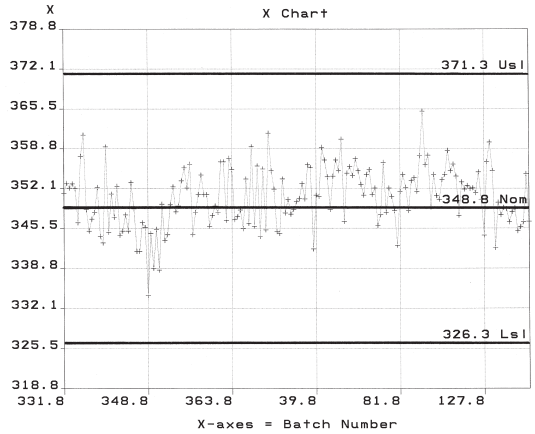

Figure 2. First line control for starch in corn silage. Y-axes = starch ($g * kg^{-1}$).

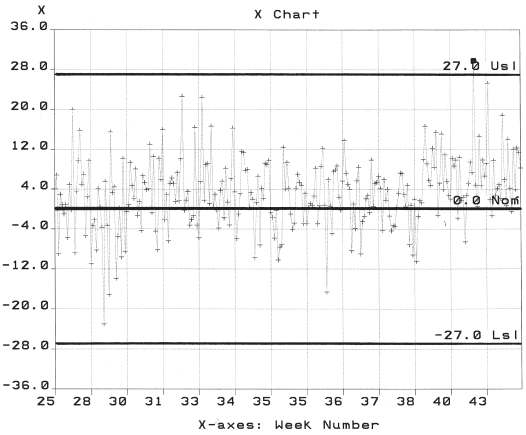

Figure 3. Moving validation. Y-axes: crude protein in grass silage (g ∗ kg^{-1} DM).

The nominal value is set at the historical average value for the instrument noise. The lower control limit is resulting from the upper control limit and the nominal value.

Figure 1 shows that the instrument noise is in control. The graph shows, too, that around the end of April the instrument noise decreases a bit. This improvement is due to maintenance of the air-conditioning unit.

First line control

In Figure 2, a Shewhart chart of the first line control for starch predicted in corn silage is shown. This graph contains data from almost half a year (from the beginning of December, day number 331, to the end of May). The nominal value (348.8 g • kg^{-1} OM) is calculated as the average starch content predicted from the NIR spectra of check samples analysed before the calibration is introduced. The control limits are calculated as ± 3 × .5 × 15 the nominal value (15 is the $RMSEP_{goal}$ value for starch in corn silage, see Table 1).

From Figure 1 it is clear that the starch calibration is in control during this period. There are some minor cases of drift, but these will not have a distinctive influence on the quality of the reported starch content.

Moving validation.

In Figure 3 a Shewhart chart of the moving validation of crude protein in grass silage is shown. Because the response values in the graph are calculated as crude protein predicted minus crude protein determinated, a positive response is a result of an over estimated protein content by NIR. The nominal value is zero and the control limits are set at three times $RMSEP_{goal}$ value, this is ± 3 × 9 = ± 27 g• kg^{-1} DM. The limits for the bias are calculated as 0.5 times $RMSEP_{goal}$.

Using a moving validation information is plotted not only from the NIR analysis system, but also about how well the calibration performs on newly harvested samples. Figure 3 shows that the protein content was slightly over estimated (+ 3 g • kg^{-1} DM). At the end of the season (from week 38) the protein is even overestimated by approximately 6 g • kg^{-1} DM. Additionally, the random variation descends during the season. The larger residuals were caused by samples of the first cut from 1998. These samples where quite special, containing a low fibre content. Material like this was not well represented in the calibration database, causing larger residuals.

The samples selected for the moving validation form a representative validation set. This data set can be used as an independent data set for selecting and validating new calibration models.

Conclusion

A Shewhart chart is a powerful tool to monitor an analytical process. Not only first line control but also monitoring the performance of an instrument and validation of a method in time can be applied using a Shewhart chart. Even when the process is in control, changes in the process can be detected, like drift in average or variance.
The use of predefined prediction errors ($RMSEP_{goal}$) makes quality control clearer.
This quality control system has made a important contribution in receiving an ISO Guide 25 accreditation for our NIR analysis system.

References

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