NIR analysis of agricultural products in ring tests - experiences from the network of the VDLUFA

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Ring tests were conducted to determine the precision of NIR analysis in a network. For the analysis of rapeseed, forage maize and grass silages networks of NIR instruments have been created. The precision of NIR analysis in these networks were compared to the analysis with reference methods to determine the analytical potential of NIR analysis under the given conditions.

Material and methods

Ring test samples

For the ring tests sample material was collected from commercial seeds (rapeseed), plant trials (forage maize) or farmers and experimental stations (grass silages). Forage maize and grass silages were dried (60°C) and ground (1 mm sieve) prior to sample splitting. In 2000 the forage maize samples were distributed unground to test for the effect of decentralised grinding on the reproducibility.

Sample splitting was done using appropriate splitting devices for ground material (forage maize and silages) or whole seed kernels (rapeseed).

Ring tests

The first ring tests for rapeseed analysis using NIR was conducted in 1995 with 10 samples (Tillmann *et al*. 1997).[1] Two samples of grass silage were distributed in a ring test in 2000 (VDLUFA 1999ff.).[2] Ring tests for forage maize analysis were conducted since 1999 (VDLUFA 1999ff.).[2] In these ring tests NIR analyses were done on all samples (n = 4–8), reference methods on 2–4 samples per year only to reduce the work load. For each ring test 4 analyses had to be done per sample.

The ring test data were analysed according to ISO 5725[3] using a C program. The C program was validated using data from the literature (Tillmann 1997).[4]

The repeatability standard deviation of a method (σ_r) is the standard deviation of test results on identical test items by the same operator in the same laboratory using the same equipment within a short interval of time (repeatability conditions, ISO 5725).[3] The reproducibility standard deviation of a method (σ_R) is the standard deviation of test results on identical test items by different operators in different laboratories using different equipment and the same method (reproducibility conditions, ISO 5725).[3]

NIR measurements

All NIR measurements used in these ring tests were done on instruments run in a network. The network and its calibrations are described in Tillmann[4,5] and Tillmann *et al*.[1,6]

Reference analysis

In all ring tests to which data are presented here the reference analyses were done on the same samples or part of them. The reference methods are named in the tables and legend and described in detail in VDLUFA (1997).[7]

Table 1. Ring test rapeseed 1995 (*n* = 10).

Constituent / (Range)	Method	*N*	P	σ_r	σ_R
XL	Soxhlet	15–20	4–5	0.28	0.71
(45.4–50.4% DM)	NMR	35–40	9–10	0.19	0.91
	NIR	51–52	13	0.36	0.66
GSL	HPLC	15–20	4–5	0.86	1.09
(7.9–16.7 μmol g^{-1} DM)	XRF	11–12	3	0.77	3.37
	NIR	50–52	13	0.83	1.96
XP	NIR	51–52	13	0.28	0.40
(18.3–22.9 % DM)					

Results and discussion

The results from the rapeseed ring test from 1995 are presented in Table 1. The data from the silage ring test are presented in Table 2.

Table 2: Ring test silages (*n* = 2)

Constituent	Method	σ_r	σ_R
XP	4.1.1	0.14	0.40
	NIR	0.21	0.54
XF	6.1.1	0.16	0.37
	NIR	0.06	0.12
XL	5.1.1	0.23	0.65
	NIR	0.15	0.47
XZ	7.1.1	0.43	1.03
	NIR	0.23	0.37
ADF	6.5.1	0.42	1.37
	NIR	0.77	1.51
NDF	6.4.1	0.19	0.51
	NIR	0.20	0.30
Gb	25.1	0.65	1.57
	NIR	0.35	0.77

P = 10–16 for reference methods, P = 9 for NIR method

Data from forage maize ring tests are presented in Table 3 grouped by constituent. In 2000 the reproducibility of analyses decreased markedly for NIR and reference methods. This is most likely not the result of decentralised grinding but more likely of sample heterogenity. Otherwise systematic differences for all samples dependent on the grinder used should have been observed.

Judged by the presented data sample splitting of a product that consists of two separate fractions (ears and stover) with a particle size of 20–30 mm is more than difficult.

Table 3. Ring tests forage maize (*n* = 2–8).

Constituent	Year / (Range)	Method	p	σ_r	σ_R
XS	1999	7.2.1	14–15	0.2	1.1
	(16.0–32.8%)	NIR	24	0.6	1.0
	2000	7.2.1	6–11	0.3	3.0
	(19.5–35.4%)	NIR	17–20	1.0	2.2
	2001	7.2.1	10–12	0.3	1.2
	(15.7–27.3%)	NIR	23–25	0.9	1.6
	2002	7.2.1	9–12	0.3	1.1
	(3.8–33.9%)	NIR	30	0.7	1.2
Cellulase	1999	6.6.1	14	0.5	1.4
	(65.0–69.0%)	NIR	21–24	0.5	0.7
	2000	6.6.1	8–13	0.6	3.3
	(64.6–69.7%)	NIR	15–20	1.0	1.4
	2001	6.6.1	10–12	0.5	2.4
	(63.6–68.4%)	NIR	23–27	0.9	1.2
	2002	6.6.1	10–13	0.6	1.7
	(62.0–67.9%)	NIR	30	0.7	0.8
XF	1999	6.1.1	14	0.3	0.8
	(19.3–22.3%)	NIR	23–24	0.4	0.9
	2000	6.1.1	8–13	0.4	1.2
	(16.8–21.7%)	NIR	18–20	0.5	1.3
	2001	6.1.1	10–11	0.3	1.0
	(19.9–23.1%)	NIR	23–27	0.5	1.0
	2002	6.1.1	12–13	0.2	0.6
	(18.8–25.1%)	NIR	30	0.3	0.6
XP	1999	4.1.1	13	0.07	0.2
	(6.2–6.9%)	NIR	17–24	0.08	0.2
	2000	4.1.1	7–13	0.1	0.3
	(5.8–9.3%)	NIR	18–20	0.1	0.2
	2001	4.1.1	11–12	0.08	0.4
	(6.2–7.8%)	NIR	25–27	0.2	0.3
	2002	4.1.1	9–13	0.07	0.2
	(6.6–7.8%)	NIR	30	0.1	0.2

Conclusions

In a pairwise comparison neither the reference methods nor NIR analysis is superior in repeatability or reproducibility. A slight tendency for better precision under repeatability conditions

is evident for the reference methods. On the other hand a slight tendency for better precision under reproducibility conditions for the NIR methods.

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Abbreviations

n = number of samples in ring test
N = number of single analyses
P = number of laboratories
all data in % DM, except GSL in μmol g^{-1} DM and Gb in ml 200 mg^{-1} DM
σ_r = repeatability standard deviation
σ_R = reproducibility standard deviation
4.1.1 Kjeldahl, 6.1.1 Weende Analysis, 6.4.1, 6.5.1 van Soest, 6.6.1 de Bouver, 7.1.1 Luff-Schorl, 7.2.1 Ewers, 25.1 HFT (VDLUFA 1997)

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