Proficiency testing and certified reference material as a basis for standardisation of near infrared/near infrared transmittance methods

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Introduction

The changes in the metrological view of measurement results over the last 90 years and the widespread use of accreditation proceedings, as well as the ISO 9000 quality assurance systems, lay claim to new requirements for in-laboratory quality assurance systems regarding accurate measurement of objective and unified qualification. Expectations have increased on the administrative side of laboratory work—documented methods, standards, unified uncertainty estimations—and on the technical side—documented calibration and certification of the devices, regularly made inner and outer audit, which ensure control of every little piece of laboratory work.

For legal certification of the value of a quality or quantity parameter, the traceability to the national or international standards should be assured. This means that the measuring equipment used in the laboratory should be compared with working standards.[1] There is a special type of working standard: *Certified Reference Material (CRM)*, which is able to validate a measuring process and calibrate an instrument. The accredited laboratory has to use CRMs to control the validity of the measurement method, the device, the calibration and to improve them.

The Chemical Section of OMH[2] have embarked on the preparation of a series of wheat samples as CRMs. The certification processes are carried out accordingly to ISO recommendations.[3]

Wheat is the most widely cultivated plant in Hungary. Therefore wheat production is an important determining factor in the Hungarian economy. This is why its objective and unified qualification is of great importance. In wheat trading the price determining parameter is its inner composition. Both the buyer and the seller are interested in having an accurate standardised measurement. At present the results of the classical testing methods are used for fixing the price.

The laboratories have to investigate a large number of samples during a short period of time during the wheat harvest and hoard. This means that a number of instruments are required, (compared to previous times)—including the fast testing near infrared/near infrared transmission (NIR/NIR transmittance) instruments.

In case of the buying and selling wheat, the following combined parameters are used to calculate the price; moisture, protein, wet gluten content, the falling number and the water absorption. There are fixed standards to determine these qualifying parameters.

An accredited laboratory network with sufficient experience is available for investigation. Most of these laboratories use NIR/NIR transmittance instruments as the first step for determining moisture, protein and wet gluten content before using the time-consuming classical measurements. Mehtods and

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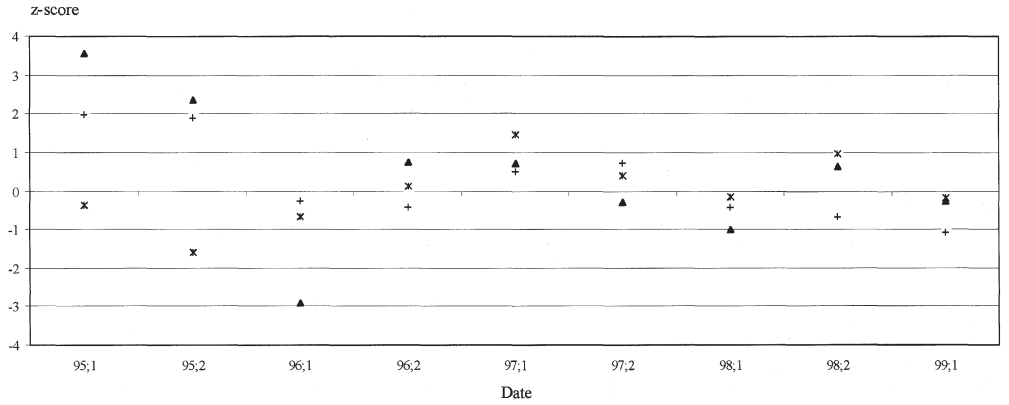

Figure 1. Z-score values of NIR/NIR transmittance protein content determination (11.Lab).

results from laboratory measurement reports are uncertain. In the case of NIR/NIR transmission methods the results can just be indicated values. The (legal) metrological control can use the results of these measurements as the basis for price fixing parameters.

Proficiency testing

The National Office of Measures (OMH) extended its activity, together with the Proficiency Testing Organisation, to fulfil the previously mentioned objectives, as well. Taking part *in Proficiency Testing* helps the laboratories to compare their own measuring results with other laboratories' results.

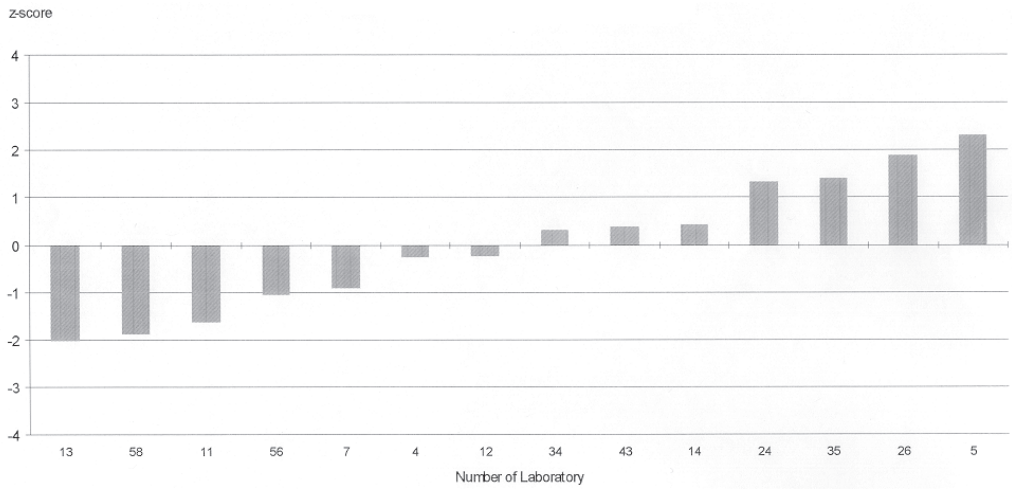

Figure 2. Z-score values of NIR/NIR transmittance wet gluten content determination (3.wheat sample in 1999/1 proficiency testing).

This interlaboratory testing makes it possible to unify the different measuring methods and to test their reliability to establish the value of their traceability, reproducibility and accuracy.

OMH has organised proficiency testing twice a year—fall and spring time—since 1994. All participant laboratories receive 3-3 different wheat grain and wheat flour samples from the same sample mass, respectively, in the fall and in the spring (Figure 1). In this way we can investigate the changes of the different parameters in the sample during storage under normal laboratory conditions, too.

Laboratories measure the standardised wheat parameters which are used for the wheat qualification and the NIR/NIR transmittance moisture, protein and wet gluten content. The participant laboratories only need to take measurements in which they have sufficient experience for the satisfying evaluationof the interlaboratory testing.

Evaluation of the proficiency testing

The evaluation is performed according to ISO-GUIDE 43[4] *Proficiency Testing* by Interlaboratory Comparison 1–2. The laboratories are classified based on the resulting "z-score" values (Figure2).

Participation is currently voluntary for the laboratories. Every laboratory gets a code number at the final report.

The data treatment steps are as follows:

$$z = \frac{\bar{x}_l - X}{\sigma}$$

Where,

$$x_l = \frac{\sum_{i=1}^{n} x_i}{n} \qquad \bar{X} = \frac{\sum_{I=1}^{N} x_I}{N} (\Rightarrow X)$$

z: z-score value

$\hat{X}$: *true value*, this value comes from the evaluation of the classical measurement results in case of NIR/NIR transmittance measurement

σ: target value for standard deviation

x_i: replicate determination results

n: number of replicates

$\bar{x}_l$: mean of replicates within laboratory

$\bar{X}$: between laboratory average

N: number of participant laboratories

σ: the target value for standard deviation was chosen to conform with Hungarian Standards.

The calculated z-score of laboratory measurement clearly shows the direction and the extent of the deviation of the laboratory result from the consensus value. If the z-score value is > ± 3 of any measurement the laboratory has to improve the performance for which our samples are efficiently used (Table1).

The long term z-score results of NIR/NIR transmittance measurements show that, in gen-

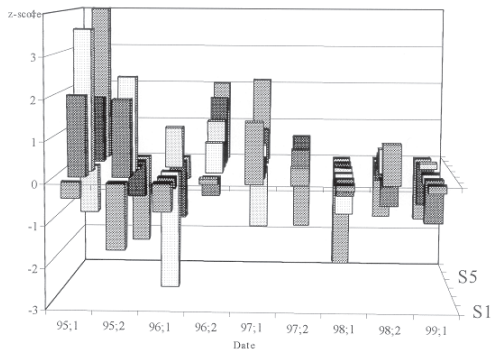

Figure 3. Z-score values of NIR/NIR transmittance protein (S1–S3) and wet gluten (S4–S6) content determination (11.Lab).

Table 1. Result of NIR/NIR transmittance determination (1999) wet gluten content.

1 wheat			2 wheat			3 wheat		
Laboratory number	[%]	z	Laboratory number	[%]	z	Laboratory number	[%]	z
4.	32.0	–0.17	4.	27.1	1.09	4.	23.6	–0.28
5.	32.7	0.50	5.	27.6	1.74	5.	25.5	2.30
7.	31.9	–0.24	7.	27.2	1.21	7.	23.2	–0.91
11.	32.3	0.15	11.	25.3	–1.08	11.	22.7	–1.64
12.	32.7	0.54	12.	27.2	1.29	12.	23.7	–0.24
13.	31.4	–0.84	13.	24.9	–1.64	13.	22.4	–2.03
14.	34.0	1.93	14.	24.9	–1.54	14.	24.1	0.43
24.	30.9	–1.34	24.	25.8	–0.42	24.	24.8	1.33
26.	32.5	0.38	26.	26.8	0.78	26.	25.2	1.88
34.	31.8	–0.43	34.	25.9	–0.42	34.	24.1	0.32
35.	32.6	0.44	35.	26.9	0.95	35.	24.8	1.41
43.	32.0	–0.18	43.	23.9	–2.91	43.	24.1	0.37
56.	32.2	–0.02	56.	26.6	0.57	56.	23.1	–1.05
58.	31.5	–0.72	58.	26.4	0.37	58.	22.5	–1.89
$\bar{X}$:	31.5	—	$\bar{X}$:	26.1	—	$\bar{X}$:	24.3	—
mean:	32.2	—	mean:	26.2	—	mean:	23.8	—
st dev:	0.8	—	stdev:	1.08	—	stdev:	1.0	—
max:	34.0	1.93	max:	27.6	1.74	max:	25.5	2.30
min:	30.9	–1.34	min:	23.9	–2.91	min:	22.4	–2.03
σ	1.0	—	σ	0.79	—	σ	0.7	—

Symbols:
$\bar{X}$ [%(M^{-m})]: average of laboratory results
z: final z-score value
$\bar{X}$: average of laboratory results by standard method
σ: target value for standard deviation

eral, interlaboratory testing has improved the speed of calibration each year (Figure 3).

Participation in the proficiency testing twice a year and regular calibration control with CRMs provides continous and direct relationship between the classical and NIR/NIR transmittance methods.

Notes and references

1. Hungarian Law on Legeal Metrology No XLV. (1991).
2. Measures and Services of the National Office of Measures (OMH) (1998).
3. ISO GUIDE 35. Certification of Reference Materials-general and Statistical Principles (1989).
4. ISO GUIDE 43-1-2: Proficiency Testing by Interlaboratory Comparisons.

5. Certified Reference Material is a special type of working standards, which is able to validate a measuring process, to calibrate an instrument. This means the measuring equipment used in the laboratory should be compared with a working standard.
6. The purpose of Proficiency Testing makes it possible to unite the difference measuring methods and to test their traceability and reproducibility and accuracy.

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