Continuously measurement of the dry matter content using near-infrared spectroscopy

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Abstract: Near-infrared spectroscopy (NIRS) was used in agriculture and food chemistry in the early 1960s. NIR is located at a wavelength range between 800 nm and 2,500 nm. Although NIRS technology is a rapid, repeatable, highly precision and environmentally friendly technology for recording of spectra without destroying the samples, it is a complex method and the spectrometer calibration with a validated primary reference analysis is required. This study aimed at testing the suitability of NIRS for documenting the dry matter (DM) content of the stored silage in plastic bags. Accordingly NIRS sensors were installed in a commercial silo bagging machine after preliminary experiments in small scale were done. Maize and grass silage DM content was detected continuously using NIRS during storage process. The mean reference values for maize silage were significantly 6.6% higher than the NIRS values. With grass silage, NIRS values were only 0.6% below the mean reference value. The results of the NIRS sensor in the grass silage bag were less uniform than those of the maize silage due to no continuous direct contact between the measuring window and the substrate. NIRS sensor proved generally to be a suitable means of determining the DM in the crop flow of the pressing machine. However, continuous contact between the ensiled material and the NIRS sensor must be ensured, to guarantee that measurements are correct.

Keywords: Near-infrared spectrometer, maize and grass silage, dry matter content, bagging machine

1 Introduction

The infrared spectrum of the electromagnetic spectrum is located between the visible light and the microwaves at a wavelength of between 800 nm and 10,000 µm. Infrared spectrum is divided into three further areas: the far infrared (FIR), the middle infrared (MIR) and the near infrared (NIR). NIR is located at a wavelength range between 800 nm and 2,500 nm (Günzler and Gremlich, 2003; Workman and Shenk, 2004; Sandorfy et al., 2007; Otto, 2011; and Manley, 2014).

The area of near-infrared light was discovered over 200 years ago by the astronomer Sir Frederick William Herschel in 1800 (Siesler, 2002; Workman and Weyer, 2012; Manley, 2014; and Prieto et al., 2017). The principle of near-infrared spectroscopy (NIRS) has been known for over 100 years. In the early 1960s, NIRS was used in agriculture and food chemistry (Ferrari and Quaresima, 2012; Manley, 2014). Thereafter, NIRS has become one of the fastest growing analytical techniques in the world after evaluation of the electromagnetic radiation using multivariate chemometric techniques in the 1970s (Manley, 2014).

Rapidity, repeatability, highly precision and environmentally friendly recording of spectra without destroying the samples is one of the main advantages of the NIRS (Büning-Pfaue, 2003; Dieterle et al., 2003; Zhang and Su, 2014; Quentin et al., 2017; and Prieto et al., 2017). In addition, the costs per measurement are significantly lower than with conventional methods (Quentin et al., 2017). Furthermore, the installation of the devices is

relatively easy and inexpensive to implement and promise a long shelf life (Williams, 2007; Prieto et al., 2017).

The disadvantage of this method is the complex, but indispensable calibration of the spectrometer with a validated primary reference analysis (Büning-Pfaue, 2003; Dieterle et al., 2003; and Prieto et al., 2017). Since the reference samples are usually wet-chemically analyzed, good calibration become very costly (Prieto et al., 2017).

The absorption of electromagnetic radiation causes atoms in the molecules to be set into mechanical vibrations in the region of the near infrared (Pasquini, 2003; Günzler and Gremlich, 2003). It can also lead to transitions of several vibration levels, which are named as harmonics or overtones and have a multiple of the fundamental vibrations (Bokobza, 2002). In contrast to the MIR, the NIR does not observe the fundamental vibrations but their harmonics (Workman and Weyer, 2012). The bands of the NIR are mainly based on OH, CH, and NH bonds, because here the conditions of light atoms with strong chemical bonds are fulfilled (Prieto et al., 2017). Their fundamental vibrations occur between 4,000 and 2,000 cm^{-1}, so that their overtone bands are above 4,000 cm^{-1} (Bokobza, 2002; Günzler and Gremlich, 2003; and Sandorfy et al., 2007).

Basically, there are two different ways to measure in the near-infrared range. On the one hand it is measured in the mode of transmission, on the other hand in the (diffuse) reflection. The transmission measurement is usually used for the liquids (Tsuchikawa, 2007) and reflection for solid materials like silage. With respect to all spectroscopic methods used for the quantitative evaluation, the Lambert-Beer law (Ebel and Roth, 1987; Workman and Springsteen, 1998) applies in principle.

The aim of this study was to investigate the suitability of NIR spectrometer measurements technique for determining the dry matter content of the stored silage in plastic bags. Thus, NIRS sensors were used to measure and record the DM content of the substrate continuously during the storage process in small and large scale experiments.

2 Material and methods

2.1 Preliminary experiments for NIRS sensor calibration

In this investigation, the used NIRS (tec5 company, Germany) consisted of the measurements head (model NIRON II) and a spectrometer system (model AgroSpec 1.7). The measuring head on which the measurement took place was equipped with a sapphire crystal. The measured spectrum was transferred to the spectrometer via a fiber optic cable and was processed. Then the measurement was reached to a process computer via a serial interface. Special software (MultiSpec Pro, tec5 company) was used to process the spectral data. Preliminary experiments were conducted to calibrate the NIRS for DM of chopped fresh maize and grass (Figure 1). The calibration was carried out using 110 and 108 samples form maize and grass respectively. Some samples were dried in an oven from 40% up to 70% DM in order to achieve a higher variability of the samples. Due to the heterogeneity of the substrate, an average of ten individual spectra was used for each silage sample. Ten measurements as number of cycles were moved over the measuring head in 5 seconds, thus the cycle time was 0.5 s and the number of scans was 15. The integration time was 21 ms and measuring type was absorption.
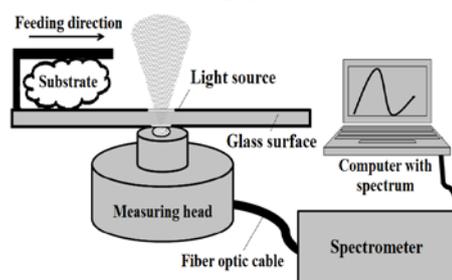
Figure 1 Structure for the samples presentation chain on the measuring head for calibration

A mean spectrum value was formed from the 10 spectra and a relevant reference value was assigned. A sufficient amount of 250 g substrate was lightly pressed to avoid any gab between the light source and the silage. The analyzed sample was then weighed and dried in a drying oven according to the method provided by VDLUFA (2012). The reference values to the respective spectra were assigned. The follow-up took place with the softwares "CalibrationWorkshop" and "Utilities" while the actual calibration and validation was done using CalibrationWizard software. These sofwares were obtained from SensoLogic Company. At the end an equation was

created with CalibrationWizard software to calculate DM content of the substrate directly by NIRS. After the calibration under laboratory conditions, it was possible to use the NIRS with commercial silage bagging press machine.

2.2 NIRS sensor instillation on a commercial silo bagging machine

The calibrated NIRS sensor was installed in the silo bagging machine (Figure 2). The measuring head was mounted on the tunnel rear wall to face the material flow. The measuring head and connected fiber optic cable were very well protected against mechanical effects. The spectrometer was placed outside the machine with rubber buffers to be protected against the shocks and vibrations. The position of the measuring head at this point was advantageous because the substrate to be ensiled there already flowed compactly along the sapphire glass of the head and thus there was permanent contact between the silage and the light source during the whole working process.
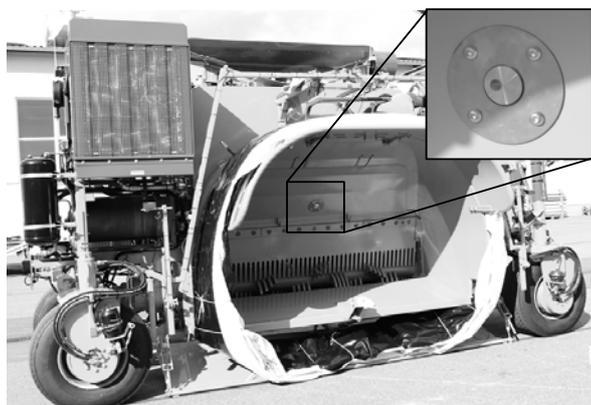
Figure 2 Location of the NIRS measuring head in the tunnel rear wall of the silo bagging machine

2.3 Statistical analysis

The significant differences of the data were done using Analysis of Variance "ANOVA" using SPSS software. To assess a calibration quality, different performance measures are calculated in the quantitative analysis. These provide information on how to classify the values obtained on the basis of the reference and predicted values in the NIRS (Büning-Pfaue et al., 1998; Büning-Pfaue and Kehraus, 2001; Williams, 2001; Davies and Fearn, 2006; François et al., 2009). Standard Error of Calibration (SEC) was calculated as the standard deviation of all NIRS estimated-values from the reference values. The standard error of the prediction (SEP) indicates to the difference between the NIRS estimated values and the reference values of the validation samples. The quotient of the standard deviation of the reference values for the validation samples and the standard error of the prediction represents the Ratio Performance Deviation (RPD) for comparative evaluation of the calibration models. The RPD values reflect the calibration quality as mentioned by William (2014).

The BIAS is the mean systematic error by which all validation samples are over- or underestimated on average. According to Aurich (2009), the values should be close to zero or not more than 0.6 times the SEC value. With the root mean square error of prediction (RMSEP) only some of the samples are used to calculate the calibration function. The other part, called the test set, is validated by the already determined calibration. The NIRS values of the test set samples are compared with the reference values.

3 Results

3.1 Preliminary experiments for NIRS calibration

The NIRS sensor was calibrated for detecting the DM content of both maize and grass silage in the laboratory experiment. The investigated substrates were stored during practical experiments and were analyzed at the same time for their DM content by the sensor. DM content for maize ranged between 23%–68% while 80% of DM values ranged between 25%- 45%. For grass silage, DM content ranged between 18%–81% and 49% of the sample size ranged between 25% and 45%. DM contents of more than 45% were produced by pretreatment of the samples in the oven in order to increase the variability within the sample set for the calibration. The spectra of each sample were recorded and then merged into an average spectrum. The absorption was visible at wave length range of 1,160 to 1,450 nm. For calibration, 80 mean spectra of each silage were analogously selected from Calibration Wizard software program while 20 additional spectra were used in the experimental set for subsequent validation. The calculated R^2_{cal} from predicted and actual DM values was 0.94 and 0.95 for maize and grass silage respectively (Figure 3). Other evaluation

relevant parameters of calibration and validation for both   maize and grass silage are presented in Table 1.

(a) maize   (b) grass
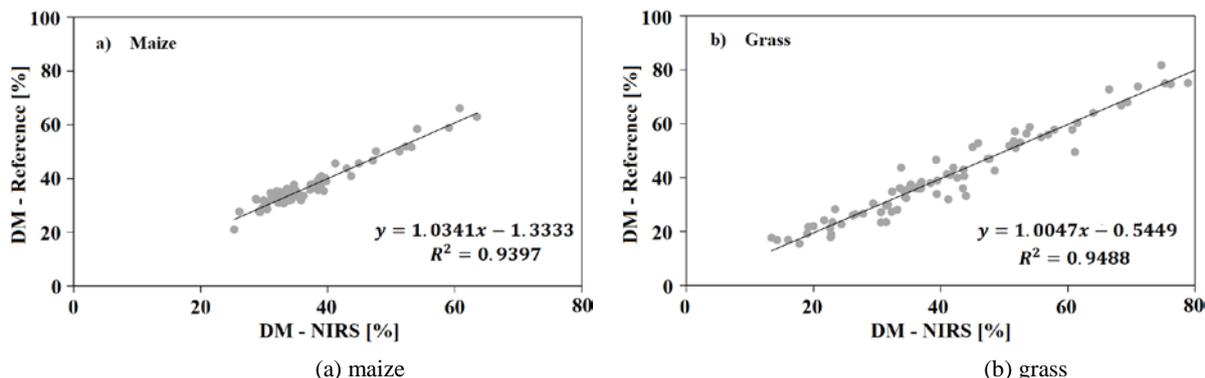
Figure 3 Correlation between the NIRS measuring value and the reference sample for maize (a) and grass (b)

Table 1 Analysis values of the DM calibration and validation for maize and grass silage

	Maize silage	Grass silage
SEC	2.3	4.7
SEP	3.6	11.7
RPD	2.8	1.9
BIAS	0.5	0.5
RMSEP	3.6	11.4

3.2 DM content determination by NIRS

The DM content for silage was determined during the storage process with the previous calibrated NIRS sensor installed on the tunnel rear wall of the commercial silo bagging machine (30 m). The obtained data was recorded with one second intervals on the process computer. DM content was measured between 33%–45% for maize and 20%-40% for grass silage. Samples for DM reference values determination were withdrawn from sixteen measurement positions throughout the bag with 1.5 m intervals. Reference measurements samples were taken in the mid-dle bag area as well as from both sides but not in the direct start and end areas. NIRS recorded the average values of DM content per one running meter of silo bag. The NIRS values for maize silage were in the range of 32.0% to 35.7% DM over the total bag length, with an average ± standard deviation of 33.4% ± 1.1% DM. The reference levels varied between 38.1% and 43.4% DM with average 40.0% ± 1.5% DM. The mean reference values were significantly 6.6% higher than the NIRS values. However, an approximately parallel trend of the two measurements over the whole bag length was observed (Figure 4a). The results of the NIRS sensor in the grass silage bag were less uniform than those of the maize silage (Figure 4b). NIRS average value was 28.5% ± 4.1% DM, with only 0.6% below the mean reference value (29.1% ± 2.1%). Consequently, a significant difference in the DM determination methods was not identified.

(a) maize   (b) grass
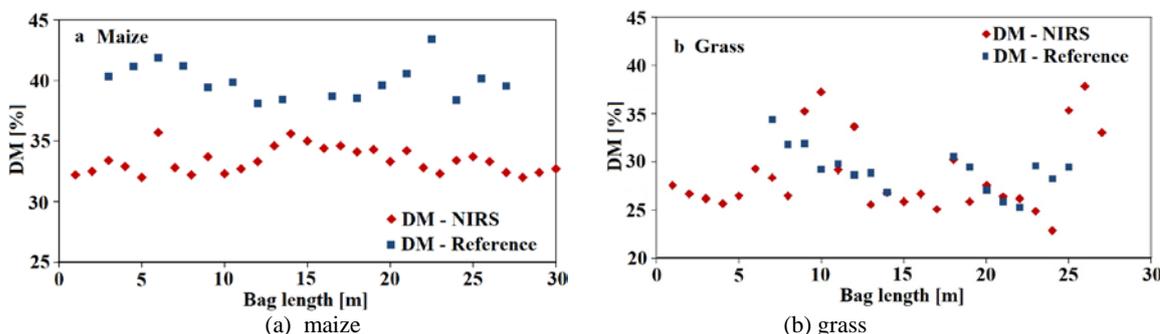
Figure 4 Relationship between the determined DM content of NIRS and reference samples for maize (a) and grass (b) silage

4 Discussion

The used NIRS sensor was calibrated and installed behind the tunnel to be protected from external influences.

4.1 Installation of NIRS sensor

The integrated NIRS sensor was protected against external influences and had no contact with the folded bag.

The location of NIRS sensor installation was intentionally chosen on the back wall.

The wear due to substrate friction was significantly increased at this position. There was a permanent contact between the silage and the built-in measuring window of the NIRS sensor due to the assumption that the material flow at this position was a highly compressed.

4.2 Assessment of the NIRS calibration

The laborious calibration of the NIRS sensor in the laboratory was unavoidable before using in the commercial silage bagging press machine. In order to ensure a significate measurement prediction of the DM content, it was necessary to check the calculated statistical parameters and, if necessary, subsequently correct to the calibration. An actual comparison of the most relevant parameters presented in Table 2. However, the aim of this work was not only to create an optimal calibration, but also to prove whether the general use of a NIRS sensor in a silo bagging press machine is possible and useful.

With a correlation (R^2) between the spectra and the reference values of 0.94 (maize) and 0.95 (grass), the values were slight below the target value as recommended by Williams (2001).

The RMSEP describes the test set validation and specifies the relationship between the values from the test set and the reference values. The value of maize was 3.6 while the value of the grass deviates more sharply (Table 2).

RPD value is one of the most important indicators to assess the calibration and describes the relationship between the standard deviation of the reference values of the validation samples and the standard error of the prediction (Williams, 2001).

Table 2 Comparison of the NIRS calibration parameters and target values

	Actual values		Target values
	Maize	Grass	
Number of samples	110	108	25 (Mark, 1991) > 30 For agriculture Substrate (Agelet and Hurburgh, 2010) 20-30 (Williams, 2001) Difficult to estimate due to the number of latent variables (ASTM, 2005)
R^2_{cal}	0.94	0.95	0.96 (Williams, 2001)
SEC/SEP in %	63.9	40.2	Close to100
RPD	2.8	1.9	Close to 8.0 (Williams, 2001) Close to 4.0 u.a. For fodder (Williams, 2014)
BIAS	0.5	0.5	Close to 0
RMSEP	3.6	11.4	Close to 0

As shown in Table 2 and according to the significant prediction of the NIRS presented by Williams (2014), the calibration of maize silage DM can be classified as satisfactory while the calibration of the grass silage DM is insufficient.

The DM distribution in the maize silage bags was recorded by NIRS at the time of storage and varied according to the properties of the substrate (Figure 4a). Although the reference values showed a parallel trend, these values were significantly higher by an average of 6.6% DM (p <0.05) and contradict the statistical assessment of the calibration. However, a modification of the calibration function by a correction factor indicated a higher accuracy of the prediction.

The deviation returns to various reasons. The DM content of the harvested maize silage was unexpectedly high > 40% which could not be predicted during laboratory calibration. A high number of dry samples with 40% DM content led to smaller deviations. Another reason may be the number of latent variables (ASTM, 2005), so that the samples number of 110, contrary to the statistics, was insufficient. There was no way for connecting the calibration to the field use during the preliminary experiments with the test bagging press machine and it had to be relocated to the laboratory.

In the case of DM detection in the grass silage bags, there was a higher correlation in the measured values. Here, the difference between the DM contents of the NIRS sensor and the reference sample was only 0.6% and was insignificant. This accordance was unexpected after the statistical evaluation of the calibration and contradicts in content. In particular, the problem with determining the DM values during the storage of grass silage, that there is no continuous direct contact between the measuring window and the substrate due to the existence of the vertical layer.

As a result, there were often incorrect values which have to be removed by the software filter. With regard to maize silage, this was predominantly the case when idling in the press occurred after unloading a transport vehicle. In future, such a data filter should always be programmed directly in the developed software so that only valid values of the NIRS sensor are recorded.

The developed calibration models in this study showed first positive results and provide a good basis for the DM prediction of NIRS sensor. In further investigations the number of samples should be expanded. The installation of the NIRS sensor in the machine and especially in the tunnel rear wall is possible on principle. In the future after this successful calibration, further ingredients can be determined in addition to the DM content.

5   Conclusion

The main objective of this study was to figure out the possibility of determining the DM content in silage flow during storage process using NIRS technology. The integration of NIRS sensor in a silo bagging machine was in principle possible and suitable for DM detection in the silage flow. Batch storage in bag allows partial disclosure of information, which in the future can provide the farmers with information about the currently available silage. However, a permanent contact between the silage and the measuring window of the NIRS sensor must be ensured in order to avoid incorrect measurements. Only DM content of the silage during storage in bags was determined. In particular the calibration for DM determination of silage was conducted in order to optimize the prediction accuracy.

Acknowledgment

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Nomenclature

Symbol and abbreviation	
DM	Dry matter content
NIRS	Near-infrared spectroscopy
R^2	Coefficient of determination
SEC	Standard Error of Calibration
SEP	Standard error of the prediction
RPD	Ratio Performance Deviation
BIAS	Systematic error
RMSEP	Root mean square error of prediction