Prediction of Fermentation Qualities of Baled Corn Stalk Silage with Near Infrared Reflectance Spectroscopy

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Abstract Near infrared reflectance spectroscopy (NIRS) was evaluated as a tool to predict the chemical compositions of baled corn stalk silage. A total of 112 samples were used for determination of the pH value, crude protein (CP), crude ash (CA), dry matter (DM) and soluble carbohydrate (WSC). Samples were scanned with near infrared reflectance spectrometer and partial least-squares regression (PLSR) was used to predict the chemical compositions. The coefficients of determination of calibration (R^2) and the coefficients of determination of validation (R_V^2) of the pH value, CP, CA and DM were higher than 0.85. The relative percent differences (RPD) of the pH value, CA and CP were higher than 2.5. The RPD of the WSC was higher than 2.0, and its R_V^2 was 0.72. Therefore, the NIRS can provide accurate prediction of the pH value, CP and CA. It can also provide relatively accurate prediction of DM, but the variation range of DM should be enlarged. Moreover, it can be used for a rough estimate of WSC, but the precision should be improved.

Key words Near infrared reflectance spectroscopy; Baled silage; Corn stalk; Fermentation qualities; Calibration model; China

Corn stalk is a kind of feed, and it is generally stored with silage technology. Silage with whole stalks is different from the conventional method. Whole stalks are wrapped tightly and kept at a high density. After they are bagged and air is completely exhausted, the baled silage comes into an anaerobic state in a short time, so that the stalks are well fermented by lactobacilli. If the fermentation is good and no air enters the bag, the stalks can be stored stably for a long term.

The large-scale and intensive production of silage is enlarging, and higher requirements are proposed for quality and safety of livestock products, thus quality inspection of silage is becoming the issue of universal concern from researchers at home and abroad. Furthermore, determination of chemical compositions is an important part of evaluation on silage quality[1]. The traditional methods are time-consuming and laborious and also require chemical reagents and higher operating techniques. Near infrared reflectance spectroscopy (NIRS) has rapid analysis, simple sample preparation, convenient spectroscopy, and good reproducibility[2], thereby it is ideally suitable for rapid determination of multiple components of plant. Since the late 1980s, the NIRS has been widely used, and now it has been an important means to evaluate crop quality in foreign countries[3-8]. To develop a rapid method to evaluate stalk qualities, we used the NIRS to determine pH value and content of common chemical compositions such as dry matter (DM), crude protein (CP), crude ash (CA) and soluble carbohydrate (WSC) of corn stalk silage.

1 Materials and methods

1.1 Collection and preparation of samples A total of 112 samples of corn stalk silage were collected from different regions of Shaanxi Province from April 2008 to July 2009. These samples had different pretreatment methods (fermentation with or without additives) and different fermentation methods (baled silage with whole corn stalks or traditional drum silage). After fermentation for 60 d, the silage was dried in an oven at 65 ℃ for 48 h. After it was crushed with Fw135 high-speed universal grinder (Taisite Instrument; Tianjin, China) and screened through 1.0 mm sieve, the powder was sealed in a plastic bag.

1.2 Determination of chemical compositions The pH value was determined with pH meter. The CP content was determined by the Kjeldahl method (GB 6432-86). The DM content and the CA content were determined by the AOAC official method[9]. The WSC content was determined by anthrone – sulfuric acid colorimetric method[10]. There were two duplicates in parallel. The content was based on DM.

1.3 Spectral acquisition Near-infrared spectra were acquired by a VECTOR22/N Fourier transform near infrared spectrometer (Bruker Analytik; Karlsruhe, Germany). Preprocessing was done on the total spectral region (12 000 and 4 000/cm), and 64 scans were averaged at a resolution of 6.0/cm. To diminish differences arising from size, each sample was scanned three times, and the average was used for data analysis.

1.4 Establishment of quantitative calibration model Optimization of quantitative calibration model, preprocessing of spectrum, spectrum selection, and regression analysis were performed with OPUS/QUANT5.5 software for quantitative analysis. The quantitative calibration model was developed using partial least squares (PLS) and mathematical pretreatment methods such as smooth, derivative, standard normal variate-detrended (SNV-D) and multiplicative scatter correction (MSC). To avoid over-fitting, full-cross validation was performed. In addition, the number of principal components was determined, and validation was performed with an independent

Received: November 23, 2009 Accepted: December 5, 2009
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sample test set. Abnormal spectral values were checked with Mahalanobis' distance, and chemical values were checked with absolute error[11]. The optimal model was selected according to coefficients of determination of calibration (R^2), standard error of cross validation (SECV), standard error of calibration (SEC), and standard error of prediction (SEP)[12-13].

2 Results and analysis

2.1 Chemical compositions of silage Table 1 shows the pH values as well as the content of the chemical compositions of the corn stalk silage.

Table 1 Chemical composition and pH values of corn stalk silage

Items	Minimum	Maximum	Mean	Standard deviation
pH	3.56	4.97	3.96	0.68
CP	45.38	188.71	85.77	14.21
CA	56.59	108.50	80.46	18.52
DM	272.46	477.18	356.89	40.21
WSC	4.18	38.81	14.98	4.72

The content of the chemical compositions (g/kg·DM) are based on DM.

2.2 Near-infrared reflectance spectra of corn stalk silage All the 112 samples of corn stalk silage were scanned with the near infrared spectrometer. Fig. 1 shows that the spectrum of the sample is typical, and it has multiple absorption peaks within the whole wavelength range. Therefore, the spectra provided enough information for quantitative analysis on the chemical compositions of the corn stalk silage.

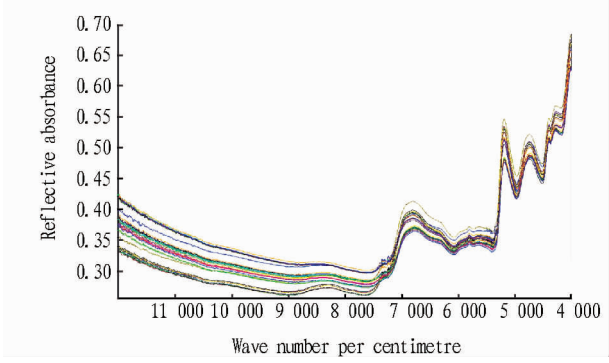

Fig. 1 Near infrared spectrum of dried corn stalk silage

2.3 Development and validation of calibration model Abnormal samples were eliminated using Mahalanobis' distance according to results of outlier test. Then the optimal preprocessing of the spectrum, spectral range, and number of the principal components were determined.

As can be seen from Table 2, different qualities of the silage had different optimal modeling conditions. Using the parameters in Table 2, the near-infrared calibration models were developed for each quality trait. In these modeling conditions, R^2 was the highest, and the SECV was the lowest.

Table 2 Parameters of near-infrared calibration models for quality traits of corn stalk silage

Indexes	Number of abnormal samples	Number of samples for calibration	Number of samples for validation	Mathematical treatment method	Number of principal components
pH	2	83	27	The 1st Deriv. + SNV	8
CP	5	80	27	The 1st Deriv. + MSC	7
CA	0	85	27	The 2nd Deriv. + SNV	7
DM	4	82	26	The 1st Deriv. + SNV	8
WSC	0	85	27	Detrend only	8

SNV. Standard normalized variate; MSC. Multiplicative scatter correction.

The calibration models of the pH value, CP content, CA content, DM content and WSC content had higher R^2. The rate of prediction to deviation (RPD) of the pH value, CP content and CA content was higher than 2.5. Moreover, coefficient of determination of validation (R_V^2) was higher than 0.85. These results showed the developed calibration model may be used for good measurement of the pH value, CP content and CA content. Fig. 2 shows correlation between the measured pH value and the chemical pH value of the samples for validation.

The R^2, SECV and R_V^2 of DM were respectively 0.93, 17.71 and 0.90 (Table 3), which indicated the developed calibration model for DM may be used for good measurement of the DM content (Fig. 3). However, the RPD was lower than 2.5, possibly because the DM content did not change greatly, that is, the range of the DM content was narrow[14-15].

The R^2, SECV, R_V^2 and RPD of WSC were respectively 0.81, 2.21, 0.72 and 2.14, which showed the calibration result of WSC was not very satisfactory. The NIRS did not meet the requirements of quantitative analysis on the WSC content, thereby it can be only used for a rough estimate of WSC. The precision should be improved.

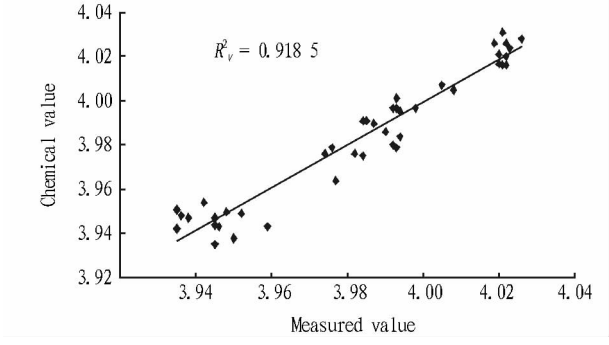

Fig. 2 Correlation between the measured pH values and the chemical pH values

In addition, the SEP of each component was higher than the SEC, which showed the predicted values was not as accurate as the calibration results[16].

Table 3 Calibration and validation of chemical compositions of corn stalk silage

Indexes	Calibration model					Validation		
	R^2	SEC	R^2_{CV}	SECV	RPD	R^2_V	SEP	Slope
pH	0.95	0.12	0.93	0.14	4.85	0.92	1.17	0.92
CP	0.91	3.87	0.88	4.84	2.93	0.85	6.83	0.85
CA	0.93	5.11	0.90	6.71	2.76	0.88	7.26	0.90
DM	0.93	14.65	0.91	17.71	2.27	0.90	19.02	0.87
WSC	0.81	1.89	0.78	2.21	2.14	0.72	4.43	0.76

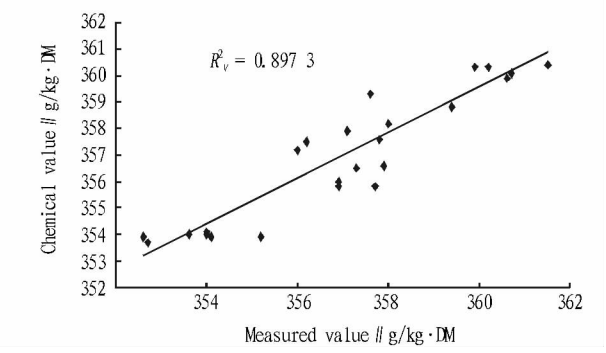

Fig. 3 Correlation between the measured DM content and the chemical DM content

3 Discussion

Among the methods to analyze quality traits of corn stalk silage, the NIRS has such advantages as simultaneously analyzing many different components, rapid analysis and high accuracy that the conventional chemical methods do not have. The NIRS can provide accurate prediction of the pH value, CP and CA. The RPD of DM was lower than 2.5, thereby the variation range of DM should be enlarged by using more samples in follow-up studies, and calibration results for DM should also be further confirmed. Moreover, it can be used for a rough estimate of WSC, but the precision should be improved to meet requirements of quantitative analysis.

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基于近红外光谱的玉米秸秆捆包青贮饲料的品质测定研究

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摘要 以112个玉米秸秆整杆捆包方式青贮的饲料为试验材料,利用近红外漫反射光谱技术,结合偏最小二乘法,对捆包青贮饲料的pH值、粗蛋白(CP)、粗灰分(CA)、干物质(DM)和可溶性碳水化合物(WSC)含量进行测定和分析。结果表明,pH值、CP、CA和DM的校正模型决定系数(R^2)以及外部验证决定系数R^2_V均大于0.85,且pH值、CA和CP的相对分析误差RPD(SD/SECV)均大于2.5。WSC的RPD大于2,外部验证决定系数R^2_V为0.72。近红外漫反射法可以很好地测定捆包青贮样品的pH值、CA和CP含量。测定DM含量时,需进一步扩大样品含量变异范围。该方法也可对WSC含量进行粗略估测,但精度有待提高。

关键词 近红外漫反射光谱;捆包青贮;玉米秸秆;品质测定;校正模型