Prediction of the degradability and ash content of wheat straw from different cultivars using near infrared spectroscopy

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ABSTRACT

Degradability of straw is important in connection with the fermentation process for bioethanol production, while the ash content is important for its suitability for incineration. Therefore, a fast method for assessment of straw quality could be very useful in determining the price and in helping choose between different applications for specific straw batches, such as fermentation for ethanol production, incineration or animal feed. This study investigated the ability of near infrared (NIR) spectroscopy to predict the degradability and ash content of 106 cultivars of wheat straw grown at two different sites. In general, calibrations based on NIR spectra recorded on air-dried samples performed better than those on oven-dried samples. A partial least squares (PLS) calibration based on the spectra of the air-dried samples predicted degradability with $r^2 = 0.72$ and $RMSECV = 1.4\%$ with 3 components using samples from the two different sites. The ash content was well predicted with $r^2 = 0.99$ and $RMSECV = 0.195\%$ using a complex 15-component PLS model validated using repeated random segmented cross-validation. However, this model proved to be sensitive to site in a validation using the two sites as segments, where the accuracy of ash content prediction decreased to $r^2 = 0.91$ and $RMSECV = 0.691\%$ using a 9-component PLS model. NIR spectroscopy proved useful for predicting degradability and ash content of wheat straw from different wheat cultivars. However, when developing predictive models of ash content based on NIR spectra, it should be ensured that the models are transferable to locations other than those used for model calibration.

1. Introduction

During recent decades, biomass has increasingly been seen as a resource that can replace fossil fuels in the energy sector and chemical industry. Wheat (*Triticum aestivum* L.) is one of the major crops in the world, resulting in the production of large amounts of wheat straw, which can potentially be used for these purposes. However, there are also a number of traditional uses of cereal straw, such as animal feed and bedding.

There are large differences in degradability between wheat straw produced at different locations and from different cultivars (Kernan et al., 1984; Tan et al., 1995; Jensen et al., submitted). This is important both in terms of the value of the straw as a feedstuff and for some of the biological processes for bio-fuel production, such as enzymatic saccharification and fermentation to produce bioethanol.

A range of different degradability assays have been developed to assess different aspects of degradability of different organic matter samples. These assays are designed to assess degradability under standardised conditions so that the results can be compared between laboratories, but they are expensive and laborious. Therefore, near infrared (NIR) spectroscopy has been suggested as a rapid and non-destructive method to replace these reference methods. For straw from different cultivars of the same crop, calibrations between degradability and NIR spectra have been established for maize stover (Melchinger et al., 1986; Zimmer et al., 1990) and for grass (Nordheim et al., 2007; Ohlsson et al., 2007), while calibrations between NIR spectra and chemical composition have been established for rice straw and maize stover (Pordesimo et al., 2005; Jin and Chen, 2007). For barley, a NIR calibration predicting potential degradability of the straw was presented by Mathison et al. (1999), but to our knowledge no previous attempts have been made to relate the NIR spectra of straw from different wheat cultivars to their degradability.

The ash content is also important for the usefulness of the straw. A high content of alkali metals associated with the ash causes problems with corrosion, slagging and fouling during incineration and

other processes for energy extraction from the straw (Michelsen et al., 1998). After incineration, the ash can serve as a fertilizer, whereas it may constitute a waste product for disposal if it contains undesirable elements (Mozaffari et al., 2000). NIR spectroscopy has already proven its potential for determination of the ash content of plant materials (Vázquez de Aldana et al., 1996; Ruano-Ramos et al., 1999) and animal feeds (Dahl et al., 2000). A similar calibration for rapid determination of the ash content of wheat straw could be very useful for determination of the quality and the potential use of the straw.

After straw has been collected in the field and stored, it still contains some water depending on the weather, storage conditions and characteristics of the straw. The water bands found in the NIR spectra are a composite of the different hydrogen-bonded subspecies and therefore the degree of hydrogen bonding influences the apparent position of the water bands in the NIR spectrum (Shenk et al., 2001). Oven-drying the samples before NIR analysis may therefore be advantageous because it reduces and ideally equalises the water content of the samples.

The main objective of the current paper was to investigate whether NIR spectroscopy can be used as a fast and cheap method to assess the degradability and ash content of straw from a wide range of current Northern European wheat cultivars. A secondary objective was to test whether oven-drying the straw before NIR analysis improved the calibrations compared with air-drying.

2. Materials and methods

2.1. Collection of straw

Wheat straw was collected straw from 106 cultivars at two different sites near the towns of Sejet (55°49′12.43″N and 9°55′21.82″E) and Abed (54°49′40.05″N and 11°19′30.62″E) in Denmark. Both sites are part of a series of official field trials comparing different cultivars of winter wheat. The cultivars included a range of different commonly grown and new cultivars adapted to the growing conditions of north-west Europe.

Approximately 80 g of straw DM were sampled from each plot by taking four to five handfuls from different places in the plots. The straw was ground on a cyclone mill (President, Holbæk, Denmark) fitted with a 1 mm screen.

2.2. EFOS assay

Degradability of the straw was assessed with the EFOS assay, using a modified version of the method described by de Boever et al. (1986). The assay was carried out as described by Weisbjerg and Hvelplund (1993) but modified by replacing the original Gammanase and Novozym 188 with Novozym 51454. A subsample of approximately 0.5 g of each of the milled straw samples was incubated in a filter crucible with 30 ml pepsin–HCl solution for 24 h in a 40 °C water bath. The crucibles were then transferred to an 80 °C water bath and incubated for 45 min. After this, the samples were washed twice with 20 ml of de-mineralised water and incubated with 30 ml of enzyme acetate buffer at 40 °C for 24 h and at 60 °C for 19 h. After the last incubation the samples were washed twice with 20 ml of boiling water and twice with 20 ml of acetone. Finally, the crucible was dried at 103 °C for 12 h, weighed, ashed at 525 °C for 6 h and weighed. The soluble fraction was determined as the loss of dry weight in the material divided by the dry weight at the beginning corrected for ash content.

2.3. NIR spectroscopy

Two sets of subsamples were taken from each of the milled straw samples. One set was not dried any further (i.e. air-dried), while the

other was oven-dried at 80 °C. The air-dried samples contained on average 6.16% (w/w) water with a standard deviation of 0.75%.

Spectra of all samples were recorded on a NIRSystem 6500 (FOSS Tecator, Copenhagen, Denmark) spectrometer running in reflectance mode. The spectral range of the instrument is from 400 to 2500 nm at 2 nm intervals. The spectrophotometer uses a split detector system with a silicon detector between 400 and 1100 nm and a lead sulphide (PbS) detector from 1100 to 2500 nm. It uses a tungsten halogen lamp and has an internal ceramic standard. The light falls on the sample at an angle of 90° and here the NIR/VIS spectra were measured in reflectance mode at an angle of 45°. The NIR/VIS reflection spectra were recorded using a rotating 36 mm Ø sample cup with a quartz window. Sixteen spectra collected from different sections of the cup were averaged and converted to $\log_{10}(R^{-1})$ units.

2.4. NIR calibration

In order to explore the variation in the spectroscopic data, a principal component analysis (PCA) was carried out. Subsequently, partial least square (PLS) regressions predicting the ash content and EFOS values from the NIR spectra of both the air-dried and oven-dried samples were performed using the LatentiX software (version 2.0, Latent5, Copenhagen, Denmark, www.latentix.com). For the current samples, the visible range from 400 to 1100 nm appeared noisy and only the spectral range from 1100 to 2500 nm was used for all calibrations. A range of different methods for transforming the spectra were tested, including multiple scatter correction (Martens et al., 1983), standard normal variate (Barnes et al., 1989), Extended Inverse Multiplicative Signal Correction (Martens et al., 2003) and second order Savitzky–Golay derivatives (Savitzky and Golay, 1964). Different levels of smoothening using moving average and larger segment and gap sizes of the Savitzky–Golay derivatives were also tested.

All PLS models were validated using two different cross-validation schemes: repeated random cross-validation (RRCV) using 5 segments and 20 drawings, and site-segmented cross-validation (SSCV) using two segments defined by the two growing sites. The latter validation scheme was applied in order to assess the transferability of the calibration models from one site to another. The validation was used to determine the optimal number of components to be included in the PLS model and assessed the quality of the calibrations. Only validated performances of PCA and PLS are reported and PLS performance are given in the fraction of the explained variance (r^2) and the root mean square error of cross-validation (RMSECV).

3. Results and discussion

The straw cultivars exhibited much variation in degradability, as reflected by EFOS values ranging from 25.8% to 40.7% (Table 1). The degradability of the straw from Sejet was higher, with a mean EFOS value of 33.8% compared with 31.6% for Abed. The ash con-

Table 1
EFOS values and ash content of 106 cultivars collected at two different experimental sites, Sejet and Abed. SD: standard deviation; *n*: number of samples; SD$_{Ref}$: standard deviation of reference methods based on laboratory replicates.

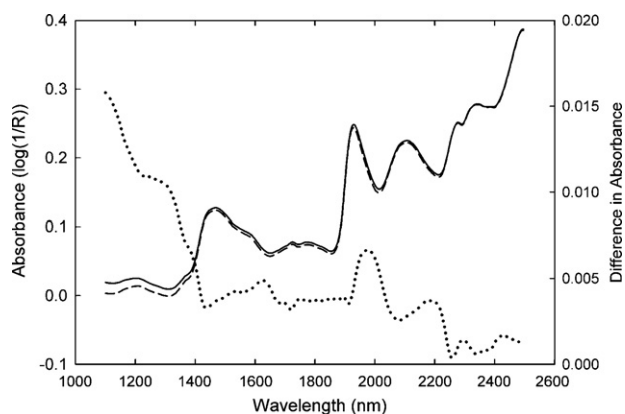|	Sejet (*n* = 106)		Abed (*n* = 106)		Both sites (*n* = 212)	
	EFOS (%)	Ash (%)	EFOS (%)	Ash (%)	EFOS (%)	Ash (%)
Mean	33.8	7.06	31.6	4.20	32.7	5.63
SD	2.4	1.01	2.6	0.40	2.7	1.63
Min	29.1	5.58	25.8	3.08	25.8	3.08
Max	40.7	11.42	38.1	5.30	40.7	11.42
SD$_{Ref}$					0.56	0.0882
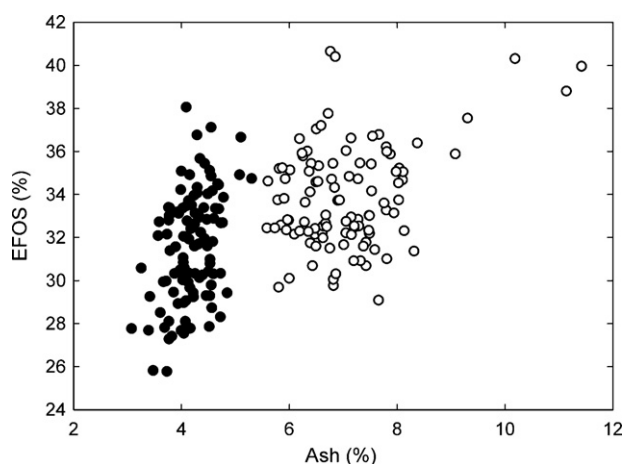
Fig. 1. Plot of ash content versus degradability as assessed by the reference EFOS assay of the samples from Sejet (open circles) and Abed (closed circles).

Fig. 3. Score-plot showing the first two principal components of the NIR spectra recorded on 212 samples of wheat straw from the two sites Sejet (open circles) and Abed (closed circles).
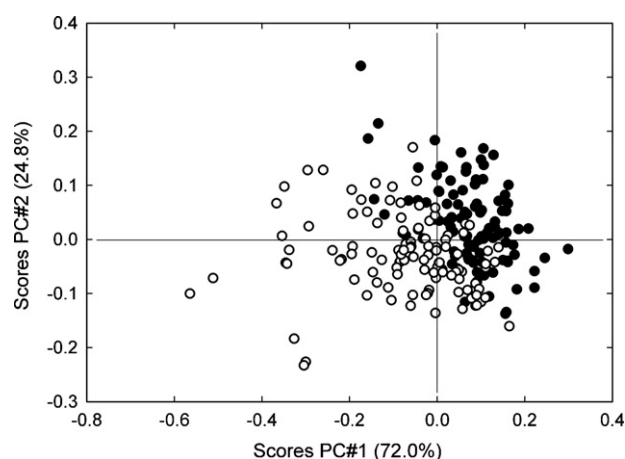
tent was significantly higher at Sejet, with a mean value of 7.06% compared with 4.20% at Abed. In particular, five samples at Sejet had high ash content (all values above 9%). Fig. 1 shows a scatter plot of ash versus degradability, which revealed no strong correlation. However the difference in ash content between the two sites is evident.

The average spectra recorded on air-dried samples from Sejet and Abed are shown in Fig. 2. There was only a significant offset in the spectra from the two growing sites in the shortwave NIR region. The first overtone of water and hydroxyl groups from cell wall polysaccharides is situated around 1450 nm, but this is hard to discern as a difference between the two average spectra in Fig. 2. The first overtone of the C–H stretches, which reside between 1600 and 1800 nm, could be indicative of dry matter content but here too, differences were difficult to discern by visual inspection. However the different spectra revealed some structure in this region. In the combination tone region from 1900 to 2500 nm in particular, the C–H stretching region near 2350 nm displayed significant structure.

The PCA score-plot of the NIR spectra is displayed in Fig. 3. The score-plot, which is plotted as a function of PC1 and PC2, represented 96% of the total variation in the data set. The sample set was obviously quite homogeneous and only a few samples to the left can be characterised as extreme. These samples proved to be those with very high ash content and it was decided to retain these samples throughout the data analysis. Finally, the score-plot shows that the two sites which were non-overlapping in ash con-

tent in the spectroscopic data tended to be segregated, but not entirely.

During the development of the PLS regressions predicting the ash content and degradability from the NIR spectra, no samples seemed to have an unduly high influence on the model so no outliers was removed from the calibration set. Smoothing progressively decreased model performance and therefore only the results of the calibrations using a minimum of smoothening are reported. All efforts to simplify the models and to select the most important intervals through interval PLS (Nørgaard et al., 2000) proved unfruitful, so only the complex but very consistent full spectral NIR PLS calibrations are reported. The calibrations developed to predict the degradability and ash content of the straw samples were generally better when they were based on air-dried samples rather than oven-dried and thus only the results of air-dried calibrations are reported.

The resulting calibrations predicting the ash and EFOS values are shown in Table 2, which also compares the different pre-processing methods of the NIR spectra, as well as the two different validation methods. Most interestingly, Table 2 shows that the PLS calibrations based on the raw spectra were practically as good as the pre-transformed models. The model complexity was quite large, using up to 21 PLS components for the ash prediction and 9 for the EFOS prediction. In fact the different pre-processing methods MSC, SNV and EISC did not significantly improve calibration performance or model complexity and only the second derivative spectra provided an improvement in model performance, in particular a reduction in model complexity. For ash, the model performance was slightly improved with a 15 PLS component model compared with the 21-component raw model. For the EFOS calibration a similar pattern was observed, but in this case only the model simplicity was improved, with the number of PLS components being reduced to three.

For the EFOS predictions, we observed very little difference between the two validation methods (*RRCV* and *SSCV*), which is indicative of a robust and transferable model. The EFOS calibration model based on second derivate spectra and *SSCV* used only 3 PLS and predicted 0.72 of the variance in the EFOS values with *RMSECV* = 1.4%. This *RMSECV* value has to be compared with the standard deviation of the reference method based on the laboratory replicates of 0.56% (Table 1), so the uncertainty of the NIR estimates was 2.5 times that of the reference method. The results of the validation are shown in the predicted versus measured plot in Fig. 4a, which is very representative of all the EFOS models. Despite the low model complexity, the PLS loadings shown in Fig. 4b reveal

Fig. 2. Average $\log(R^{-1})$ transformed reflectance spectra of wheat straw cultivars from Sejet (dashed line) and Abed (full line) and difference spectrum between the two sites (dotted line).

Table 2
Results of the cross-validation of PLS regressions used to predict the ash and the degradability of straw (EFOS) from NIR spectra of air-dried samples using different pre-processings of the spectra. The two different cross-validation schemes are: repeated random cross-validation (*RRCV*) using 5 segments and 20 drawings, and site-segmented cross-validation (*SSCV*) using two segments defined by the two growing sites. MSC is multiplicative signal correction, SNV is standard normal variate, EISC is extended inverse multiplicative signal correction and NIR 2nd is second derivative spectra using a segment size of 5 and a gap of 3.

|	Ash (%)		EFOS (%)	
	RRCV[a]	*SSCV*	*RRCV*[a]	*SSCV*
NIR RAW				
#PC	21	13	9	9
r^2	0.9835	0.9076	0.7665	0.7227
RMSECV	0.2083	0.8411	1.314	1.498
NIR MSC				
#PC	24	10	7	8
r^2	0.9866	0.8735	0.7567	0.7058
RMSECV	0.1883	0.8888	1.342	1.476
NIR SNV				
#PC	25	12	7	8
r^2	0.9870	0.9232	0.7483	0.7247
RMSECV	0.1852	0.7834	1.367	1.443
NIR EISC				
#PC	23	26	9	7
r^2	0.9867	0.9109	0.7675	0.7272
RMSECV	0.1873	0.7491	1.313	1.616
NIR 2nd				
#PC	15	9	5	3
r^2	0.9856	0.9135	0.7560	0.7322
RMSECV	0.1945	0.6911	1.343	1.419

[a] Numbers in this column for r^2 and *RMSECV* are average values for the 20 random repeats.

a quite complex pattern of underlying features and indicate that small shifts in the spectra are important. This was also confirmed by the fact that more smoothing progressively deteriorated the model performance. In comparison with our $r^2 = 0.72$ and $RMSECV = 1.4\%$, Mathison et al. (1999) predicted potential degradability of barley straw and achieved $r^2 = 0.69$ and standard error of prediction (*SEP*) = 3.64%, while Zimmer et al. (1990) assessed degradability of maize stover by an in vitro digestible organic matter assay and was able to predict these values with $r^2 = 0.88$ and $SEP = 2.24\%$ from the NIR spectra. Ohlsson et al. (2007) developed a calibration of degradability of different cultivars and species of grass with $r^2 = 0.92$ and $RMSECV = 1.8\%$. Finally, Bruun et al. (2005) predicted degradability of a wide range of different crops residues in soil with $r^2 = 0.958$ and $SEP = 5.44\%$. The calibrations presented here had poorer r^2 and better *SEP/RMSECV* than in most of those studies, reflecting the fact that the variation in degradability of the calibration set was lower than in most of those studies.

The reason for the higher predictability with the air-dried samples may be that oven-drying was unable to equalise the samples with respect to water content, or there may have been losses of volatiles and some nitrogenous compounds. In comparison, silages are usually analysed after drying because of the high water content of these forages, but to reduce the work associated with sample preparation, a number of authors have developed satisfactory calibrations on wet samples (Reeves and Blosser, 1991; Park et al., 1998). Liu and Han (2006) compared the ability of NIR to predict the chemical composition of dried and non-dried samples of straw silage and found that dried samples performed better for most variables except volatile substances. The reason why we did not observe the same improvement upon oven-drying may be because the water content of our air-dried samples (mean 6.16%, standard deviation 0.75%) was already low and less variable before oven-drying than that of the silage sam-

ples used by Liu and Han (2006) (mean 25.6%, standard deviation 6.1%).

The best prediction of the ash content based on *RRCV* validation was the calibration using the second derivative spectrum, which resulted in $r^2 = 0.99$ and $RMSECV = 0.195\%$ using 15 components (Table 2). The predictions of the model are shown in Fig. 5a. The standard deviation of difference based on the laboratory replicates was 0.0882%, so the uncertainty of the NIR estimates was 2.2-fold greater than that of the reference method. Curiously, for the ash predictions we observed a large difference in the calibration performance between the two different validation methods, *RRCV* and *SSCV*. Irrespective of pre-transformation method, the *RMSECV* was 3–5-fold greater when using the site *SSCV* validation. This indicates that there are problems with the transfer of the *RRCV*-based calibration models from site to site and therefore also outside the calibration set. The predictions of the calibration model based on *SSCV* validation are shown in Fig. 5b. The *SSCV* model predicted 0.913 of the variance in the ash values with $RMSECV = 0.69\%$. Since the standard deviation for the reference method was 0.0882%, the uncertainty of this calibration was 7.8-fold greater than that of the reference method. However, although the performance of the *SSCV*-validated model appeared poorer than that of the *RRCV*-validated model, the *SSCV* model may predict new samples from a third site better.
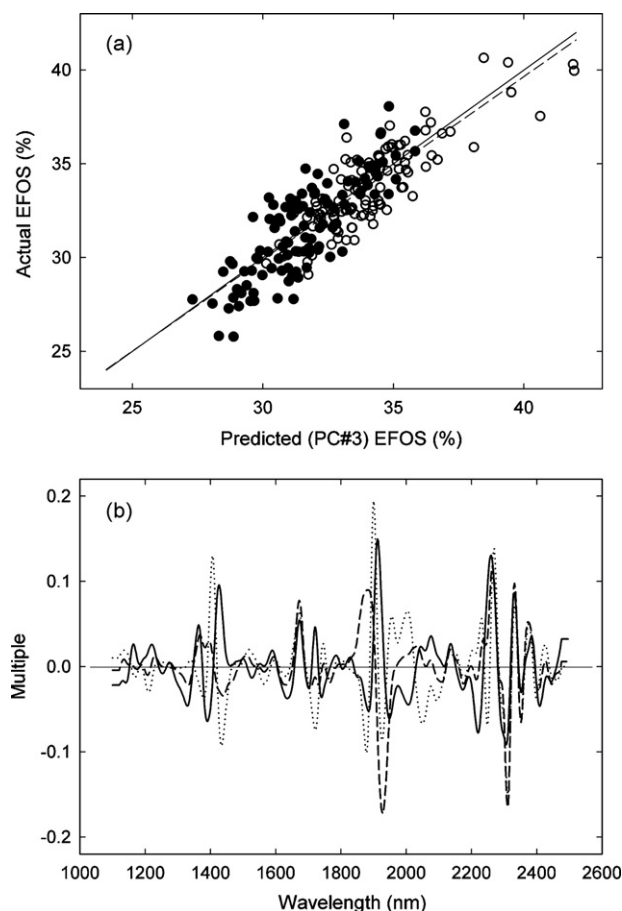
Fig. 4. (a) Comparison of predicted and measured values of straw degradability of 212 samples of straw as assessed by the EFOS assay with the regression model selected as the best. The straw came from two different sites, Sejet (open circles) and Abed (closed circles). The model was a PLS1 model transformed by a second derivative transformation using a segment size of 5 and a gap of 3. The target line of perfect agreement between measured and predicted values (solid) and a regression line (dashed) are indicated; (b) scores of the PLS component 1 (full line) PLS component 2 (dashed) and PLS component 3 (dotted) used in the PLS regression.
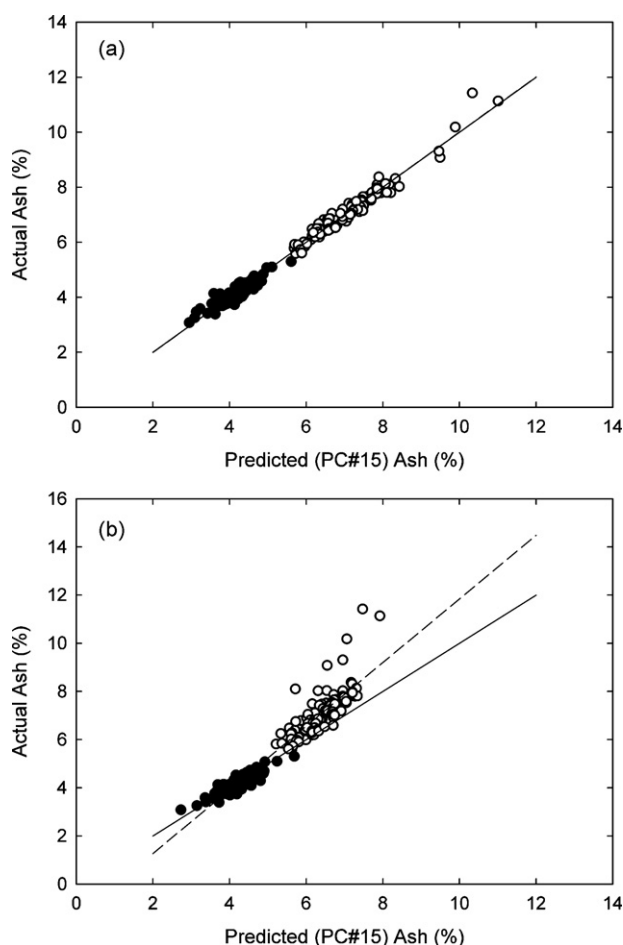
Fig. 5. Comparison of predicted and measured values of ash content of 212 samples of straw with the regression model based on (a) repeated randomised cross-validation (*RRCV*) and (b) site-segmented cross-validation (*SSCV*) using two segments defined by the two growing sites. The two sites are indicated by different open circles (Sejet) and closed circles (Abed). The models were both PLS1 models transformed by a second derivative transformation using a segment size of 5 and a gap of 3. The target line of perfect agreement between measured and predicted values (solid) and a regression line (dashed) are indicated.

Ordinarily, we would not expect NIR to be able to predict ash content, as the minerals only have indirect manifestations in the NIR range. Clark et al. (1987) successfully predicted the content of several metal cations and postulated that this was because the minerals were associated with organic molecules, which were reflected in the NIR spectra. NIR has been used to develop a range of different equations for the ash content of plant materials and forages. Windham et al. (1991) achieved $r^2 = 0.93$ and $SEP = 1.42\%$ in their predictions of the ash content of pasture and faecal samples, while Vázquez de Aldana et al. (1996) achieved $r^2 = 0.88$ and $SEP = 0.51\%$ for pasture samples. Ruano-Ramos et al. (1999) reported $r^2 = 0.85$, 0.90 and 0.82 and $SEP = 0.487, 0.354$ and 4.64 for grass, legume and forbs, respectively. The calibration techniques used in these studies were stepwise multiple regressions and it is possible that better results could have been achieved with other regression methods. Using PLS regressions, Halgerson et al. (2004) achieved $r^2 = 0.81$ and 0.91 and $SEP = 0.5\%$ and 0.5% for leaves and stems of alfalfa, while Dahl et al. (2000) achieved $r^2 = 0.98$ and $RMSECV = 0.21\%$. In comparison, the calibrations developed here to predict the ash content of straw samples were good, with $r^2 = 0.99\%$ and $RMSECV = 0.19\%$. However, the results of the more harsh *SSCV* validation where the two sites were used in each validation segment were significantly lower, with $r^2 = 0.91$ and $RMSECV = 0.69\%$. This shows that there may

be problems with transferability of the calibration sets to areas or locations other than that in which the model was developed and warrants caution when developing predictive calibration models of ash content. It is difficult to assess the degree to which previously published calibrations of ash content were hampered by transferability problems.

4. Conclusions

There are many different potential uses of wheat straw, e.g. incorporation into soil, animal feed and bioenergy feedstock. For most of these purposes degradability and ash content are important determinants of quality. We demonstrated the potential of NIR calibrations for fast assessment of degradability and ash content of straw from wheat cultivars, with an uncertainty 2–3-fold larger than that of the reference methods. Such fast assessment could be very useful in determining the price and in helping choose between different applications for specific straw batches. However, caution is needed when developing predictive models of ash content based on NIR spectra to ensure the models are transferable to other locations than those used for model calibration.

Acknowledgements

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