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Mid-infrared reflectance spectroscopy as a tool for forage feed composition prediction

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ABSTRACT

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy, in the Mid-infrared (MIR) region, has been evaluated for the prediction of chemical components in forage feeds using a modified Partial Least Squares Regression (PLSR) model. Regression regression models have been developed that predict the chemical composition from a MIR spectrum of a given forage feed sample. Data collection was carried out on 140 herbage samples consisting of 84 ryegrass - white clover samples and 56 herb mix samples containing different combinations of chicory, plantain, white clover and red clover. Several spectral data pre-treatments were explored, the best of which combined Standard Normal Variant scaling (SNV) with a first-order Savitzky-Golay (SG) spectral derivative and smoothing filter. Several of the resulting models illustrated high quality predictions (for hemicellulose, 156. 9 g / kg with a standard error of prediction (SEP_c) 19.8 g / kg, $R^2 = 0.92$, Relative Performance Deviation (RPD) = 3.54; for neutral detergent fibre, 382.8 g / kg with $SEP_c = 43.5$ g / kg, $R^2 = 0.86$, RPD = 2.60), at least on par with, or superior to, current near-infrared (NIR) methods. The SNV and SG pre-treatment almost completely reduces the contribution of strong water-based signals to the regression model, allowing the possibility of in situ prediction of forage feed composition with minimal sample preparation. ATR-FTIR spectrometers are available in a hand-held form, and the results of this research suggest that in situ forage quality analysis could be performed using MIR reflectance spectroscopy.

1. Introduction

Animal performance is affected by forage quality which in itself is determined by the chemical composition of the forage material. Knowledge of the chemical composition of different forages allows for the formulation of feeds to provide the correct balance of nutrients to meet an animal's nutritional requirements. The gross chemical composition indicates the amount of nutrients (principally energy and protein) that are available in both digestible and metabolisable form. In ruminants, this has traditionally been determined by regression models, where nutrient digestibility is predicted from gross composition data (Daccord et al., 2016), in vitro

Abbreviations: ATR-FTIR, Attenuated Total Reflectance Fourier Transform Infrared; MIR, mid-infrared; NIR, near Infrared; SNV, Standard Normal Variant scaling; SG, Savitzky-Golay; DWT, Discrete Wavelet Transform; CoV, coefficient of variation; RPD, relative performance deviation; RPIQ, ratio of performance to interquartile range

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digestibility assay (Roughan and Holland, 1977) or in situ techniques using porous bags suspended in the rumen of fistulated animals (Huntington and Givens, 1995).

However, these wet-chemical based methods can be time-consuming and expensive, therefore more rapid methods to estimate feed composition and digestible nutrient content have been developed. Near-infrared (NIR) spectroscopy has been widely used to predict gross chemical composition since the work of Norris et al. (1976) on nutrient digestibility, and the following publication of Barber et al. (1990). In the present study, the use of mid-infrared (MIR) spectroscopy to predict both forage gross chemical composition and in-vitro digestibility is investigated.

Like NIR, MIR radiation causes vibration of chemical bonds in a sample. However, MIR has several important advantages; MIR is more strongly absorbed by a sample, so will detect chemical components at much lower levels in a complex mixture, MIR is absorbed strongly by a much greater range of chemical functional groups, allowing a greater range of chemical components to contribute to the signal and a single chemical functional group absorbs a narrower range of MIR wavelengths, allowing chemical functional groups, and the chemical components associated with those functional groups to be more easily distinguished using MIR radiation. As a particularly important example, NIR is most sensitive to vibrations of bonds involving hydrogen atoms, this means NIR absorption from water strongly overlaps most of the NIR spectrum of the sample itself, and careful sample preparation and calibration is required to avoid confounding issues associated with the presence of water in biological samples. Water is a strong absorber of MIR radiation and it is often the major component in biological samples so even small variations in water content between samples can cause issues when carrying out multivariate analysis on MIR spectra of biological samples. Due to extensive hydrogen bonding water has an unusually broad lineshape (Auer and Skinner, 2008) compared to other bands in the MIR region. This unusual lineshape can be exploited using appropriate data pre-processing and filtering techniques to substantially reduce the contribution of the water signal to the sample variance, as we show in this work.

MIR spectroscopy dominates the literature over NIR for analysis of pure substances and simple mixtures and we believe that MIR should give superior performance over NIR for complex mixtures, if appropriate methods of analysis are applied. NIR has been more prevalent in applied spectroscopy due to the convenience of data acquisition by reflectance methods. Until recently, MIR spectra were mostly collected with transmission methods which are impractical for field applications due to the precise requirements on sample thickness. Attenuated total reflectance (ATR) methods have allowed acquisition of MIR spectra of biological samples in reflectance mode (Lu and Rasco, 2010) and so MIR has now acquired perhaps the most significant advantage of NIR spectroscopy. Furthermore, ATR-Fourier Transform Infrared (ATR-FTIR) instruments are already available in handheld form allowing for rapid in-field screening. Although ATR-FTIR is a reflectance method, the radiation does penetrate the sample but not to the same extent as transmission methods, thus ATR methods introduce a bias towards surface structures. The penetration depth of a typical ATR system is 2–5 μm whereas biological samples prepared for transmission studies are typically prepared with a thickness between 5–10 μm (Miller and Dumas, 2006).

Like NIR, however, for complex chemical mixtures visual inspection of a MIR spectrum will be insufficient to identify changes in chemical composition between samples. Multivariate statistical analysis is usually necessary to correlate variations in MIR spectra with variations in chemical compositions, with Partial Least Squares (PLS) regression algorithms being particularly successful.

Correlation of MIR spectra to response variables is well-known in the field of chemometrics, however, the explicit use for predicting chemical compositions of forage feeds using regression models of MIR data is not known to the authors. In this work we aim to combine the convenience of sample preparation required for reflectance-based IR techniques, with the increased specificity of MIR over the NIR spectral region. We aim to show that MIR reflectance spectroscopy can predict forage feed compositions with comparable accuracy and precision of NIR techniques but with an increased understanding of the correlations via the specific spectral information available in the MIR region. Judicious data pre-treatment is an important step in MIR chemometric analysis and we aim to show here that selection of an appropriate data pre-treatment procedure suppresses the contribution of the water signal to the sample variance and hence imparts a level of robustness to the analysis against variations in water content. Using the PLS-regression algorithm known as the *Kernel* algorithm (Dayal and MacGregor, 1997), implemented in the open-source R programming language, we aim to correlate the spectral reflectance data to several components determined via wet chemistry in two different types of herbage samples.

2. Method

A total of 140 herbage samples were used for analysis, consisting of 84 ryegrass - white clover samples and 56 herb-clover mix samples including chicory, plantain, white clover and red clover. The number of samples and the mixture of species in each sample are given in Table 1. The samples were collected in 2012, 2013, 2015 and 2016 on Massey University farms close to Palmerston North in New Zealand (40°38′S and 175°37′ E). The number of samples collected each year is also given in Table 1. The samples were frozen (−20 °C) and then freeze-dried. The freeze-dried samples were ground and sieved prior to wet-chemical analysis and ATR-FTIR spectroscopy using a Thomas hammer mill and a 1 mm screen.

2.1. Wet chemical analysis

The samples were analysed for N using the Dumas total combustion method (method 968.06, Association of Official Analytical Chemists (AOAC, 1990), and dry matter (DM) using a convection oven at 105 ^{O}C (methods 930.15 and 925.10, Association of Official Analytical Chemists (AOAC, 1990). Neutral detergent fibre (NDF) and acid detergent fibre (ADF were determined using the Tecator Fibretec System following the method described by Robertson and Van Soest (1981) (method 2002.04, Association of Official