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Predicting the heating value of solid manure with visible and near-infrared spectroscopy

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HIGHLIGHTS

- ▶ Spectral models predicted feedlot manure HHV within 1.7% with excellent reliability.
- ▶ Estimated N and S corrections to HHV reduced spectral prediction by 0.1%.
- ▶ VisNIR-DRS models reliably predicted HHV_{daf} based on proximate data within 1.8%.
- ▶ Manure-specific HHV_{daf} equations from ultimate data may improve spectral prediction.

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ABSTRACT

Visible and near-infrared spectral data were used to predict the higher heating value (HHV) and dry, ash-free HHV (HHV_{daf}) of solid manure samples collected from cattle fed diets containing wet distillers grains plus solubles (WDGS) in 0%, 15%, 30%, 45%, and 60% dry matter concentrations. The HHV was determined by isoperibol bomb calorimetry and the HHV_{daf} was calculated from an equation based on the HHV and proximate analysis. Spectral models were developed in "The Unscrambler" software. The spectral models based on all treatments with random samples withheld for validation predicted the HHV with excellent reliability within 1.7%; RMSD = 60.19 cal g^{-1} (108 Btu lb^{-1}), RPD = 2.29 (excellent), and bias = −15.29 cal g^{-1} (28 Btu lb^{-1}), using five PLS factors and identifying 129 important wavebands. Accounting for estimated N and S content reduced the predictive accuracy of the spectral models by 0.1% with an RPD = 2.28 (excellent). Spectral models based on all treatments with random samples withheld for validation predicted the HHV_{daf} with acceptable reliability within 2.0% with an RMSD = 96.17 cal g^{-1} (173 Btu lb^{-1}), RPD = 1.17 (acceptable), and bias = −19.83 cal g^{-1} (−37 Btu lb^{-1}), using five PLS (partial least squares) factors and identifying 29 important wavebands. Spectral models reliably predicted the HHV of feedlot manure with accuracy well under the 5% error margin tolerated in practical applications such as feedlot manure gasification.

1. Introduction

In the context of fuel energy, manure can be partitioned into combustible and noncombustible fractions. The noncombustible fraction contains ash and moisture which are known as the *proximate data* [1]. Ash and moisture are the primary determinants of the higher heating value (HHV) of manure, which is a measure of the gross chemical potential energy per unit of mass (cal g^{-1}, Btu lb^{-1}, or kJ g^{-1}). In previous work, we successfully predicted ash and moisture in unprocessed samples of solid cattle manure using VisNIR-DRS within 4% (db) and 3% (wb) by weight, respectively [2,3], but we do not know if VisNIR-DRS can successfully predict the combustible fraction, known as the HHV_{daf}.

The combustible fraction of manure is volatile matter comprised of complex carbohydrates, proteins, trace organic compounds, and fats, containing primarily C, H, O, N, and S. These five elements are known as *ultimate data* and are determined by *ultimate analysis* [1]. When wet distillers grains with solubles (WDGS) is incorporated in beef cattle diets, the manure-S concentration [4–6] increases linearly with WDGS inclusion rate (% DM)

Abbreviations: db, dry basis; DM, dietary dry matter; HHV, higher heating value; HHV_{daf}, dry, ash-free higher heating value; PLS, partial least squares; RMSD, root mean squared deviation; RPD, ratio of standard error of prediction to the root mean squared deviation; VisNIR-DRS, visible, near-infrared diffuse reflectance spectroscopy; wb, wet basis; WDGS, wet distillers grains with solubles.

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and may affect the HHV_{daf} of the manure. Similarly, WDGS is often higher in N than the feedstuffs it displaces in beef cattle diets [7–10]. Excess dietary N and S are excreted by cattle [11–14]. The composition of WDGS varies with the grain source, processing method, neutral detergent fiber, and ratio of wet grains to solubles [15,16]. We have shown that the inclusion of WDGS in varying proportions in cattle rations had little effect on the prediction by VisNIR-DRS of the noncombustible fraction of manure [6], but we do not know if the inclusion of WDGS in cattle diets affects the ability of VisNIR-DRS to predict the HHV and HHV_{daf} of manure.

The objectives of this study were to (1) determine the potential of VisNIR-DRS to predict the HHV of solid cattle manure using proximate data and (2) determine the effect of accounting for estimated S and N in the samples on the prediction accuracy of the VisNIR-DRS models.

2. Materials and methods

2.1. Sample collection and gravimetric analyses

We obtained 120 samples of solid cattle manure collected for a companion study [6] from beef cattle (*Bos taurus*) fed diets formulated with WDGS included at 0%, 15%, 30%, 45%, and 60% of dry matter (DM). The samples were sealed in identical plastic bags and preserved at −12 °C.

The samples were brought to room temperature and subsamples taken for gravimetric analyses of moisture and ash. The moisture content on a wet basis (% wb) was calculated for each treatment from three measurements of each subsample according to a procedure recommended for manure analysis [17]. The same subsamples were prepared according to ASTM Standard E1757-01 [18] for crude ash analysis by dry oxidation according to ASTM Standard E5865-11a [19]. Ash determination was conducted in an ashing furnace (Model F-A1730, Argo Thermodyne Co., Bangalore, India) with procedural enhancements as described in [2]. The ash content on a dry matter basis (% db) was calculated from three measurements of each subsample.

2.2. Calorimetric procedures

The HHV and HHV_{daf} values were calculated in the companion study [6] with and without HNO_3 and H_2SO_4 corrections based on the N and S fractions of the manure. An H_2SO_4 correction of 13.75 cal g^{-1} (24.75 Btu lb^{-1}) for every 1.0% S was calculated based on the heat of formation of H_2SO_4 from SO_2. This is consistent with the correction of 14 cal g^{-1} (25.2 Btu lb^{-1}) recommended by the instrument manufacturer.

A standard HNO_3 correction of 8 cal g^{-1} was automatically applied by the bomb calorimeter to account for N_2 contained in the bomb atmosphere, but this did not account for N contained within the sample material. Unlike H_2SO_4 corrections, HNO_3 corrections for N in sample material vary depending on the type of matter and on the proportions of various molecules in which N is found in the sample [20–22]. We applied an additional HNO_3 correction of 4.93 cal g^{-1} (8.87 Btu lb^{-1}) for every 1.0% N in the sample based on the heat of formation of HNO_3 from N_2. There is no standardized HNO_3 correction for manure samples, but this is a reasonable value based on those determined for cellulosic materials such as livestock feeds and bovine fecal matter [17,18].

Both HNO_3 and H_2SO_4 corrections were based on bulk mean N and S concentrations measured from treatment-wide composite samples, not the unique N and S content of the individual samples. Although current ASTM, ISO, and other standardized methods differ in their treatment of determining acid corrections, all require the titration of bomb washings [10–12]. Schroeder [22] emphasized that although sample-specific acid corrections by titration are most desirable, "average" corrections are preferred over no corrections. Titration data from bomb washings were not available in this study.

In the companion study [6], the HHV_{daf} values were calculated from the observed moisture, ash, and corrected HHV of each manure sample using the following equation:

$$HHV_{daf} = \frac{HHV}{(1-A)(1-M)} \quad (1)$$

in which HHV_{daf} is the dry, ash-free higher heating value (cal g^{-1}), HHV is the measured higher heating value corrected for N and S content (cal g^{-1}), A is the ash content (% db), and M is the moisture content (% wb).

2.3. Spectral analyses

A Field-Spec 3 spectrometer fitted with a hand-held probe (AgriSpec, ASD Inc., Boulder, CO) was used to measure reflectance of each manure sample in wavebands from 350 to 2500 nm with spectral resolutions of 3 nm at 700 nm and 10 nm at 1400 and 2100 nm. The probe featured a spot size of 10 mm and an internal halogen light source with a color temperature of 2901 ± 10 K. Reflectance was set to 100% with a Spectralon white reference panel placed inside a plastic bag identical to those containing the manure samples. The samples were scanned three times through their plastic bags, and the instrument calibration was verified after every twenty samples.

Prior to analysis by VisNIR-DRS, the samples had settled resulting in an accumulation of finer particles on the underside of the bags. When predicting moisture and ash content in previous studies, we determined that scans of unprocessed manure produced superior models than scans of dried or milled manure [2], and scans of the coarse, unsettled manure in bags strongly outperformed models built from scans of the fine, settled particles [3]. Therefore, we scanned the manure on the coarse side of each sample bag at three separate, non-overlapping locations.

2.4. Spectral data processing

The raw spectral data were processed using custom statistical computing code written in R [23] (R Foundation for Statistical Computing, Vienna, Austria) following the procedures of Brown et al. [24] as described in Sakirkin et al. [25]. Spectral models based on the first derivative of the raw reflectance predominate in published literature; however, some researchers have reported better prediction accuracy with models based on the second derivative because it effectively removes the confounding effects of particle size [26,27]. The first derivative of the raw reflectance with respect to wavelength ($\partial r/\partial \lambda$) was used in all models because we have found it to be consistently superior in predicting manure characteristics [2,3] when compared to the raw spectra and the second derivative of the raw spectra.

2.5. Model development

Partial least squares (PLS) regression models were developed in "The Unscrambler" software [28] to predict the HHV_{daf} of the samples. The models were built on mean-centered data using a segmented cross-validation PLS method and were validated with a test-set holdout. The segments for cross-validation were chosen randomly and comprised four percent of the calibration dataset. The Unscrambler uses a standard, non-linear, iterative PLS algorithm and can be allowed to determine automatically the number of factors to include in each PLS model by minimizing the residual variance of the calibration cross-validation. We permitted the