

DETERMINATION OF ASH CONTENT IN SOLID CATTLE MANURE WITH VISIBLE NEAR-INFRARED DIFFUSE REFLECTANCE SPECTROSCOPY

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ABSTRACT. Visible and near-infrared (VisNIR, 350–2500 nm) diffuse reflectance spectroscopy (DRS) is increasingly being used to quantify constituents of organic matter both in the lab and in situ. However, it is unknown if DRS can be utilized as a tool for determining crude ash content of solid cattle manure. Ash content is a significant contributor to the suitability and value of manure for use both as a biofuel and soil fertilizer, but conventional ash analysis is time-consuming and labor-intensive. In this study, we explored the feasibility of VisNIR-DRS for the rapid prediction of ash content in solid manure from beef feedyards in the southern High Plains. Proportionally mixed samples of soil and manure ($n = 201$) were evaluated for ash content by conventional analysis and then used to calibrate a statistical model for prediction of ash content by VisNIR-DRS based on multivariate partial-least squares regression and random test-set validation. Two thirds of the samples were randomly selected to build a calibration model, and the remaining third was used for validation. The coefficient of determination (r^2), root mean squared deviation (RMSD), and ratio of prediction to standard deviation (RPD) were calculated to assess the prediction model. The prediction model had an r^2 of 0.94, an RMSD of 5% ash (d.b.), and an RPD of 4. The VisNIR-DRS model successfully predicted crude ash content within $\pm 5\%$ of the observed ash content (d.b.) as determined by dry oxidation using the accepted ASTM standard E1755-01.

Keywords. Ash content, Diffuse reflectance spectroscopy, Dry oxidation, Feedlot, Feedyard, Manure, Partial least squares, PLS, Regression, VNIR, Visible near-infrared, VisNIR.

Manure is one of many biofuels and alternative energy sources being considered as a result of recent federal legislation, such as the Renewable Fuel Standard (RFS) of the 2005 Energy Policy Act, and other proposals that aim to increase consumption of biofuels. When not used as a biofuel, manure is land applied as a fertilizer. Manure quality for both fertilizer and fuel depends primarily on the ash and moisture content. Ash is defined as the mass fraction of inorganic residue remaining after dry oxidation at $575^\circ\text{C} \pm 25^\circ\text{C}$ relative to the oven-dried mass (ASTM, 2007). Moisture is defined as the mass fraction of water removed from a sample by drying at 50°C for 16 h relative to the original sample mass as collected (Hoskins et al., 2003).

Both ash and moisture are inert constituents that increase the weight of manure and composted manure while adding

little or no nutrient value (Auvermann, 1999). Since transportation costs are usually based on mass and distance hauled, ash and moisture reduce manure's net value to the end user. When manure is used as fertilizer, the adverse impact of ash and moisture is primarily economic, but when manure is used as a biofuel, the adverse economic consequences of high ash are made worse by the (1) increased fouling potential and (2) increased ash-disposal requirements (Auvermann et al., 2007). Moreover, thermochemical conversion processes are typically designed on the basis of *a priori* specifications for feedstock quality, which often include minimum thresholds for the feedstock's higher heating value (HHV). For example, a manure-fired, commercial ethanol plant in Hereford, Texas, has established a minimum acceptable fuel value (MAFV) of 6.41 MJ kg^{-1} with a maximum acceptable moisture content (MAMC) of 20% wet basis (Auvermann et al., 2007).

Moisture and ash present very different management challenges for livestock producers wishing to deliver high-quality manure as a biofuel feedstock. Within practical limits, moisture contamination is reversible: the moisture deficit in the southern High Plains facilitates passive drying during most of the year, and during wet weather patterns, partial thermophilic composting is a tactical option to accelerate drying. In contrast, once manure is contaminated with soil particles, mechanical means of removing the ash may be prohibitively expensive in both financial and net-energetic terms. A low-cost, accurate, and robust means of determining ash content in the field would provide researchers, cattle feeders, and end users with a scientific basis for improving manure-management practices, optimizing the quality and value of harvested manure, controlling land-application

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costs, and increasing the suitability of manure for use as a bio-fuel.

Visible near-infrared and near-infrared diffuse reflectance spectroscopy (VisNIR-DRS, NIR-DRS) have been in use for 30 years as a means of measuring organic constituents in various commodities such as feed, pharmaceuticals, petrochemicals, and food for human consumption (Williams and Norris, 2001). More recently, VisNIR-DRS has proven to be useful in quantifying soil constituents (Goetz et al., 2001; Udelhoven et al., 2003; Brown et al., 2005; Waiser et al., 2007), analyzing nutrients in beef, dairy, and poultry solid manures (Kemsley et al., 2001; Reeves and Van Kessel, 2000), analyzing liquid manure slurries (Malley et al., 2002; Sørensen et al., 2007), and measuring biological activity in agricultural soils (Reeves, 2001). Some studies successfully used VisNIR-DRS to determine carbon, total nitrogen, ammoniacal nitrogen, and biological activity in animal manures (Reeves, 2001; Kemsley et al., 2001; Malley et al., 2002).

VisNIR-DRS is faster (<100 ms scan⁻¹) than conventional ash determination methods such as dry oxidation (ASTM Standard E1755-01) or bomb calorimetry (ASTM Standard D5468-02). Spectroscopy is a non-destructive technique and field-portable, which lends well to both laboratory and *in situ* analyses for proximal sensing. Consequently, it has great potential for use in beef and dairy operations wherever an economic premium can be realized for incremental improvements in either fuel or nutrient density.

There has been little research on the determination of crude ash in manure by spectroscopy. Mineral constituents may be predicted by VisNIR-DRS if they are bound to or correlated with organic constituents (Malley et al., 2002; Ye et al., 2005), but attempts to determine some individual mineral constituents (such as K, Ca, Zn, and Mg) in soil and manure have not been successful (Reeves, 2001; Malley et al., 2002; Udelhoven et al., 2003; Ye et al., 2005; Saeys et al., 2005; Sørensen et al., 2007). Saeys et al. (2005) speculated that the poor prediction for some individual minerals derives from their lack of spectral activity in the VisNIR spectral range, and also because their prediction relies entirely on their correlations to compounds with spectrally active bonds (C-H, O-H, or N-H). Silica in soils is transparent to VisNIR-DRS, and soils low in organic matter have been difficult to characterize by VisNIR-DRS (Reeves, 2001). Asai et al. (1993) determined crude ash in dairy manure using multivariate regression on raw reflectance data at eight wavelengths (1680, 1778, 1818, 1940, 1982, 2208, 2180, and 2310 nm). Although Asai et al. (1993) characterized the predictive model as “highly precise,” they cautioned that more wavelengths were required to satisfactorily predict crude ash content in manure.

RESEARCH OBJECTIVES

The goal of this study was to evaluate VisNIR-DRS as a means to quantify the crude ash content of manure, using ASTM Standard E1755-01 as the reference method. Objectives were to (1) develop a VisNIR-DRS model for the prediction of crude ash in solid cattle manure, (2) determine the accuracy of the predictive model, and (3) assess the practical feasibility of VisNIR-DRS for industrial and agricultural applications.

MATERIALS AND METHODS

SAMPLE COLLECTION AND PREPARATION

We prepared a master set ($n = 201$) of manure samples to represent the full range of ash content likely to be encountered in the cattle-feeding regions of the southern High Plains. Low ash manure was collected and then adulterated with predetermined amounts of mineral soil to produce the sample set, which was subsequently divided into two subsets: one for model calibration (“calibration set”) and one for model validation (“validation set”).

The manure stock was a composite of individual samples collected by hand from randomly selected pens at three commercial feedyards in October 2007. The feedyards were under independent ownership and were located in the counties of Deaf Smith and Randall, Texas. Individual samples were collected by hand from dry areas within the pens. These samples were thoroughly hand-mixed together during collection to homogenize them.

The soil stock was a composite of samples collected at depths between 15 to 30 cm from a rangeland field located 8 km (5 miles) northeast of Canyon, Texas, in Randall County. The soil was a Pullman clay loam (fine, mixed, superactive, thermic, Torrertic Paleustoll) and is, by far, the most common soil type on which feedyards in the Texas Panhandle have been built (WSS, 2007). The soil was also thoroughly hand-mixed during collection for homogenization.

After additional mixing and coarse milling in a No. 2 Wiley mill, both the soil and manure stocks were spread separately to dry for 48 h in a greenhouse, which reached average daily temperatures of approximately 60°C. After drying, both stocks were separately hand-mixed again and then ground and sieved to a particle size of less than 2 mm to improve the repeatability of DRS scans (Kemsley et al., 2001; Malley et al., 2002).

Each of the soil and manure stocks was hand-mixed for a fourth time during the milling process to ensure maximum homogeneity and were oven-dried for 24 h at 70°C. Ash analysis was conducted by conventional means in an ashing furnace (model F-A1730, Argo Thermodyne Co., Bangalore, India) according to ASTM Standard E1755-01 (ASTM, 2007). The ash contents of the soil and the manure stocks according to the ASTM method were 95% and 32% (d.b.), respectively. This range represents the range of ash content in manure stocks found in feed yards. As a reference value, the average ash content of manure as excreted by cattle on standard finishing diets in the region was about 15.2% (d.b.) in a 12-feedyard, manure-sampling survey in 2002 (Auvermann et al., 2007).

CREATION OF TARGETED ASH SAMPLE SET

A master set of 201 samples (“targeted sample set”) was assembled, with targeted ash contents evenly distributed between 32% and 95% by mass (d.b.). The interval in ash content between successive targeted samples was 0.31% (d.b.). Each sample was created by mixing the soil and manure stocks at the appropriate mass ratios to obtain a targeted ash content. Mixture components were weighed on an electronic balance (model PE3600, Mettler-Toledo International, Inc., Zurich, Switzerland) accurate to 0.01 g. Because of differences between the two stocks’ handling characteristics, the practical accuracy was on the order of 0.1 g. The target mass for each mixed sample was 200 g.

DRY OXIDATION

Three subsamples of each targeted sample were analyzed for crude ash by dry oxidation at $575^{\circ}\text{C} \pm 25^{\circ}\text{C}$. Subsamples were prepared for ashing according to ASTM Standard E1756 by drying at 105°C for a minimum of 8 h in a drying oven (model V-31-2, Despatch Industries, Minneapolis, Minn.). The crucibles containing the samples were placed in a muffle furnace (model 650-126, Fisher Scientific, Waltham, Mass.) programmed for a four-stage oxidation sequence as follows:

1. An initial ramp rate of $10^{\circ}\text{C min}^{-1}$ to 250°C .
2. A 30 min soak period at 250°C .
3. A ramp rate of $0.5^{\circ}\text{C min}^{-1}$ to 575°C .
4. A soak period of 8 h (at 575°C).

The duration of the dry oxidation procedure from the initial ramp to the end of the last soak, plus a cooling period to return the oven to below 200°C , was approximately 20 h. Samples were then weighed on the electronic balance. Single-operator precision was $\pm 5\%$ of the mean ash content.

VisNIR-DRS

The targeted sample set was brought uniformly to room temperature from 2°C and scanned from underneath through a Duraplan borosilicate optical-glass puck containing a 20 g subsample. Each sample was scanned three times, rotating the puck 120° between each scan to compensate for any remaining heterogeneity within each sample. The VisNIR spectrometer (AgriSpec, ASD, Inc., Boulder, Colo.) measured the reflectance in wavelengths from 350 to 2500 nm with spectral resolutions of 3 nm at 700 nm and 10 nm at 1400 and 2100 nm. A scanning platform (Muglight, ASD, Inc.), featuring an internal tungsten quartz halogen light source and a platform through which the halogen light is projected, was used to scan a 1.2 cm diameter spot on each sample. A Spectralon white reference panel was used in the puck to set reflectance to 100% prior to each scanning session, and the white reference was verified after every 25 samples. For quality assurance, seven Spectralon calibration standards were scanned before and after each soil-scanning session. The standards had reflectance values of 99%, 80%, 60%, 40%, 10%, 5%, and 2%.

The raw spectral data were processed in four steps using custom statistical computing code written in R (R Development Core Team, 2006) following the procedures of Brown et al. (2006), as follows. First, because the spectrometer instrument is equipped with three sensors that detect reflectance over three distinct wavelength ranges, any discontinuities created by splicing the reflectance data at the end ranges of the sensors were corrected (see Brown et al., 2006). Second, the three raw reflectance scans for each sample were averaged. Third, the average values were smoothed with a weighted cubic spline using 5 nm knots and a smoothing parameter of 0.05. Finally, the first and second derivatives of reflectance with respect to wavelength ($\partial r/\partial\lambda$ and $\partial^2 r/\partial\lambda^2$) were computed using the spline coefficients. The values for every 10 nm from 350 to 2500 nm for the smoothed raw data and for the first and second derivatives were recorded.

Partial least squares (PLS) regression models were developed using The Unscrambler software (CAMO, 2007) for multivariate statistical analysis and validated with a test-set holdout. For each of the three spectral data sets (raw reflectance r , $\partial r/\partial\lambda$, and $\partial^2 r/\partial\lambda^2$), 135 samples were randomly selected to comprise the calibration set. After calibration, the model was validated against the remaining 66 samples, which comprised the validation set. Statistical validation with independent manure samples was not performed. The root mean squared deviation (RMSD), coefficient of determination (r^2), and ratio of prediction to standard deviation (RPD) were calculated to evaluate model performance (Malley et al., 2002; Waiser et al., 2007).

After calibration, the model was validated against the remaining 66 samples, which comprised the validation set. Statistical validation with independent manure samples was not performed. The root mean squared deviation (RMSD), coefficient of determination (r^2), and ratio of prediction to standard deviation (RPD) were calculated to evaluate model performance (Malley et al., 2002; Waiser et al., 2007).

RESULTS AND DISCUSSION

The calibration models built from the raw reflectance data, first derivative of the raw reflectance data, and second derivative were all somewhat similar, as shown by the r^2 values of the calibration models: 0.91, 0.92, and 0.91, respectively. A calibration model using VisNIR to predict ash content in fishmeal reported an r^2 value of 0.89, which is similar to and a bit less than our ash content results (Cozzolino and Murray 2004). Though the average ash content of the fish meal was much lower (1.8%) than the manure samples in this research, and ash is not expected to show absorbance in the NIR region, VisNIR DRS seems to be consistent in predicting ash content in organic substances.

Since the first derivative calibration model outperformed the reflectance and second derivative models, the following results focus on the first derivative of the raw reflectance data ($\partial r/\partial\lambda$). The calibration model yielded an RMSD of 5% ash (d.b.), which means that roughly two-thirds of future VisNIR-DRS predictions were expected to lie within 5% ash (d.b.) (fig. 1). The RPD of the PLS regression calibration model was 4. An RPD value of 4 indicates that the calibration model is reliable and reproducible. According to Williams (2001), an RPD value of 4 indicates that VisNIR spectroscopy can be used as a reliable screening tool in commercial applications.

Validation by a test set of 66 randomly selected hold-out samples yielded an RMSD of 5% (d.b.) as well. The coefficient of determination (r^2) was 0.94, and the RPD was 4. Based on the RMSD, the accuracy of the VisNIR-DRS prediction model is as good as that of dry oxidation methods. A plot of the predicted versus measured ash content of the validation data set is presented in figure 2. Comparison of the one-to-one line to the regression line indicates little bias in

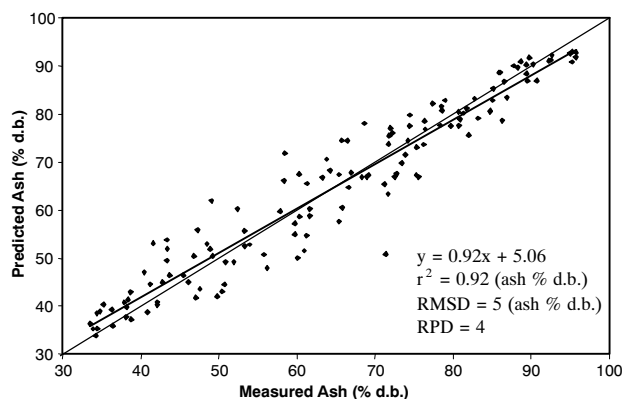


Figure 1. Predicted versus measured ash content from the calibration VisNIR-DRS model ($n = 135$) for predicting crude ash % (d.b.) in solid cattle manure. Comparison of the one-to-one line to the regression line indicates little bias in the model.

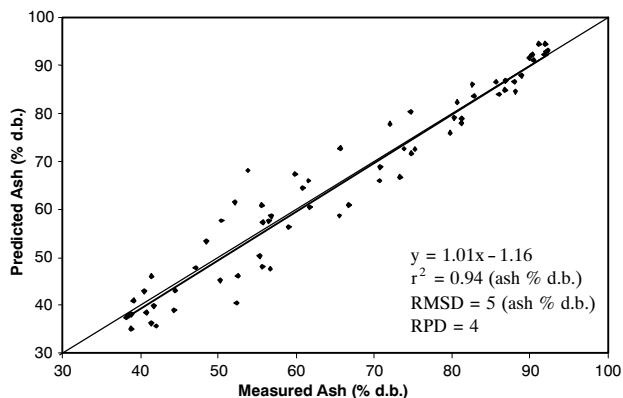


Figure 2. Predicted versus measured ash content from the validation VisNIR-DRS model ($n = 66$) for predicting crude ash % (d.b.) in solid cattle manure. Comparison of the one-to-one line to the regression line indicates little bias in the model.

the model. Although our RPD value of 4 represents validation used with non-independent samples, the high RPD is encouraging, and the result establishes a basis for continuing further tests using VisNIR detection.

The number of significant wavelengths (p -value < 0.05) for the calibration model was 23, with 7 in the visible range (350 to 700 nm), 4 in the IR-A near-infrared range (700 to 1400 nm), and 12 in the IR-B near-infrared range (1400 to 2500 nm) using two PLS factors. Table 1 presents the significant wavelengths in each of those three spectral ranges. The number of significant wavelengths found in this research was much fewer than reported by Morgan et al. (2009), where 114 significant wavelengths were identified in a VisNIR-DRS model used to determine organic carbon (OC) in ground and dried soil samples. Henderson et al. (1992) reported significant wavelengths of 1955-1965, 2215, 2265, 2285-2295, and 2315-2495 in which soil reflectance responded to OC content across a variety of soil parent materials. Within soils of similar parent material, Henderson et al. (1992) reported significant wavelengths of 405-1055, 1075, 1115, 2325, 2375, 2425, and 2445-2485. Henderson et al. (1992) determined significant wavelengths using the Tukey method of multiple means

Table 1. Significant wavelengths in the predictive VisNIR-DRS model for predicting crude ash % (d.b.) in solid cattle manure.

350 to 700 nm	700 to 1400 nm	1400 to 2500 nm
350	1150	1790
360	1190	1810
390	1330	1880
410	1400	2120
430		2130
480		2140
630		2210
		2330
		2340
		2410
		2480
		2500

comparison at a probability level of 0.01. The ranges of significant wavelengths reported by Henderson et al. (1992) and Morgan et al. (2009) are similar to those found in this research. Morgan et al. (2009) reported using six to eight PLS factors, while our models used only two PLS factors. The reduced number of factors in this research is likely a result of two causes. First, this data set was not independent because the scanned samples were all created from one mixed manure and soil source; hence, the PLS model was much simpler. Second, and perhaps more significantly, the organic carbon contents of the manure samples ranged from 5% to 60%, while the organic carbon content of mineral soils ranges from 0% to 12.5%. The majority of mineral soils are usually under 3% organic carbon. Therefore, the organic carbon signatures in mineral soils are much weaker and more difficult to recognize using spectroscopy, requiring more PLS factors for prediction purposes.

Figure 3 presents the significant wavelengths indicated as vertical lines superimposed over a graph of the first derivative with respect to wavelength of an example reflectance wave in reciprocal picometers ($1 \text{ pm} = 10^{-12} \text{ m}$). The sensor splices can clearly be observed at wavelengths 1000 and 1800 nm, which do not correspond with significant wavelengths.

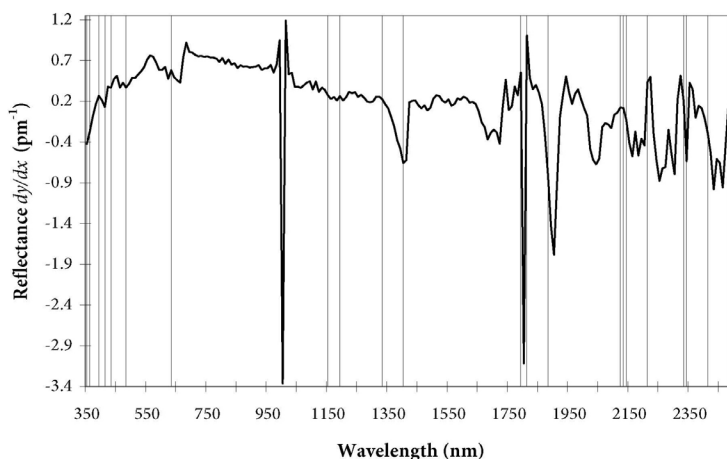


Figure 3. Significant wavelengths from the VisNIR-DRS predictive model for crude ash % (d.b.) indicated as vertical lines superimposed over a graph of the first derivative with respect to wavelength of an example reflectance wave of solid cattle manure.

CONCLUSION

Using 201 manure samples with different proportions of ash content, it was possible to determine the crude ash content of oven-dried and milled solid cattle manure by VisNIR-DRS with an RMSD of 5% (d.b.) of the observed ash content as determined by dry oxidation. This degree of accuracy is useful for quantifying the quality of manure for use either as a fertilizer or fuel.

In this study, VisNIR-DRS could determine the crude ash content of solid cattle manure as accurately as dry oxidation. These results warrant more investigations that test the robustness of this method for rapid ash determination in feedyard manure stocks. Advantages of VisNIR-DRS include rapid, non-destructive scans and portability to *in situ* analyses. Practical uses of VisNIR-DRS include on-site analysis of crude ash where manure is produced, collected, stored, and applied as either a fertilizer or a fuel.

VisNIR-DRS has also been proven to predict the moisture content of manure (Reeves and Kessel, 2000; Goetz et al., 2001; Malley et al., 2002; Brown et al., 2006); therefore, it may be possible to classify manure quality based on moisture and ash content with VisNIR-DRS. An additional model for the simultaneous prediction of moisture and ash content is required to determine the cumulative error of prediction. Practical use of such a classification scheme can be made by both users and producers of manure who are interested in knowing its fuel value and its density in relation to transportation cost.

For applications in which the precise ash content is less important than whether manure fuel value exceeds a given threshold, homogenizing, drying, and milling the samples may not be required. Scanning the manure in its *in situ* state would increase the speed and convenience of determination using VisNIR. For example, it may not be necessary to oven-dry or mill a manure sample to estimate the ash content with adequate accuracy. Further investigation is required to determine the effect of various pre-treatment protocols, such as milling vs. no milling and air-drying vs. oven-drying, on the predictive ability of the model. Once this effect is known, then the minimum pre-treatment protocol for a given degree of accuracy can be determined. The success of a faster, in-field method would greatly increase the overall utility of VisNIR-DRS in the cattle-manure context.

Because VisNIR-DRS detects the spectral signatures of bonds associated with organic molecules, the source of organic matter in the manure may affect the predictive ability of a VisNIR-DRS model built to predict crude ash content. For example, the relative proportion of corn and distillers' grains in feedyard rations (a significant variable in the feedyard industry now, given the recent growth in ethanol production in the Midwest) may be reflected in the manure's organic content. Consequently, the effect of diet composition on the model coefficients needs to be studied further. Research to determine the predictive ability of a VisNIR-DRS model based on as-collected samples of manure from animals being fed a variety of rations would prove the usefulness of VisNIR-DRS for determination of crude ash in industrial, biomass-conversion processes.

It is also possible that sample temperature influences the reflectance signature of feedyard manure. If VisNIR regression coefficients are sensitive to temperature, then field protocols will need to accommodate the temperature

dependence by preprocessing (warming or cooling the sample) or by developing unique, seasonal regression models. In the former case, the protocol will also need to account for condensation or other phase-change interferences associated with warming or cooling a sample.

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