

APPLICATION OF NEAR-INFRARED REFLECTANCE SPECTROSCOPY FOR DETERMINATION OF NUTRIENT CONTENTS IN LIQUID AND SOLID MANURES

W. Ye, J. C. Lorimor, C. Hurburgh, H. Zhang, J. Hattey

ABSTRACT. Proper application of livestock manure to agricultural land converts waste to fertilizer, but relies on knowing the nutrient content of the manure. Manure samples (111 solid poultry layer, 95 solid poultry broiler litter, 39 swine solid hoop, 72 beef cattle, 85 swine slurry, and 88 swine liquid lagoon) were collected from farms in three states to investigate the feasibility and limitations for using near-infrared reflectance spectroscopy (NIRS) to analyze manure nutrients. Spectral data in the near-infrared (NIR) region (1100-2500 nm) from manure samples were correlated with chemical analytical data from the same samples using partial least squares regression techniques in conjunction with six mathematical data pretreatments. The best calibration equations were selected on the basis of the smallest standard error of prediction (SEP) and the largest coefficient of determination (R^2) of cross-validation. The ratio (abbreviated as RPD) of the standard deviation (SD) of the constituent in the sample population to the SEP was used to evaluate the future prediction performance of calibration models. After using the mathematical pretreatments, the R^2 values of the one-out cross-validation for total solids (TS), volatile solid (VS), total nitrogen (TN), and ammonia nitrogen (NH_3 -N) were between 0.80 and 0.97 for all manure samples. The R^2 values of the one-out cross-validation for minerals ranged from 0.71 to 0.81, 0.50 to 0.78, 0.74 to 0.94, 0.66 to 0.91, 0.73 to 0.91, and 0.70 to 0.90 in poultry solid layer, poultry broiler litter, swine solid hoop, beef cattle, swine liquid lagoon, and swine slurry manure samples, respectively. The RPD values indicate that NIRS can predict TS, VS, TN, NH_3 -N, and some minerals in manures. NIRS has potential to predict some nutrient concentrations in manure rapidly and accurately.

Keywords. Animal waste, Manure, NIR, Nutrient testing.

Accurate knowledge of manure nutrient contents is crucial for land application of manure because overapplication of manure nutrients can cause environmental problems such as water pollution (Lorimor and Melvin, 1996; Prantner et al., 1999; Warnemuende et al., 1999). Overapplication may lead to environmental losses, while underapplication can result in reduced crop production. Conventional wet chemical methods of analysis for manure nutrient contents have been the norm for many years, but they are quite complicated, labor intensive, and time-consuming (Leco, 1999; AOAC, 1980). Due to increasing environmental concern from farm manures, rapid and robust methods of analyzing manure nutrient contents are necessary (Van Kessel et al., 1999; Van Kessel and Reeves, 2000).

Recently, several researchers have demonstrated that near-infrared reflectance spectroscopy (NIRS) can be used to

analyze the nutrient contents in manure samples. Asai et al. (1993) demonstrated that NIRS could be used for quick determination of total nitrogen (TN), total carbon (TC), and crude ash in cattle manure. Nakatani et al. (1996) reported that NIRS could be used to accurately measure TC, TN, ash, etc., in cattle manure compost. Millmier et al. (2000) reported that NIRS could predict total solids (TS), TN, ammonia nitrogen (NH_3 -N), and potassium (K) in swine lagoon effluent, liquid swine pit, and solid beef manure samples using raw spectral data. Reeves and Van Kessel (2000) reported that NIRS could accurately determine the moisture, TC, TN, and NH_3 -N, but not phosphorus (P) or K contents in dairy manure. Reeves (2001) also indicated that NIRS could accurately determine NH_4^+ -N, organic N, TN, and moisture, but not minerals in poultry manure. So far, most researchers have not shown that NIRS can be used to analyze minerals in manure.

In this study, mathematical data pretreatment was used to modify raw spectral data to correct the baseline, to enhance spectral data, or to assist in smoothing a spectrum. Applying mathematical data pretreatments for NIRS spectra will enhance the qualitative interpretation of spectra and the prediction ability of calibration models and optimize the calibration accuracy (Li et al., 1996). The objective of this study was to determine the feasibility and limitations for using NIRS by using different mathematical data pretreatments to analyze 11 nutrients including TS, volatile solid (VS), TN, NH_3 -N, calcium (Ca), P, K, sulfur (S), sodium (Na), zinc (Zn), and copper (Cu) in six types of manure (solid poultry layer, solid poultry broiler litter, solid swine hoop, beef cattle, swine slurry, and swine liquid lagoon).

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MATERIALS AND METHODS

SAMPLES AND CHEMICAL REFERENCE ANALYSES

Manure samples (111 solid poultry layer, 39 swine solid hoop, and 85 swine slurry) were collected from farms in Iowa. In addition, 95 solid poultry broiler litter manure samples were collected from farms in Oklahoma and Missouri, while 72 beef cattle and 88 swine liquid lagoon manure samples were collected from Oklahoma and Missouri, respectively. All samples were collected between June and November 2000. To obtain a range of constituent concentrations, samples were taken from three "layers" in the manure profile (top, middle, and bottom) where possible in different livestock facilities. For dry solid manure samples (solid poultry layer, broiler litter, swine solid hoop, and beef cattle feedlot), 1 to 2 kg samples were collected, sealed, and immediately frozen in freezer-quality Ziploc bags. For liquid manure samples (swine liquid lagoon and swine slurry), 200 mL samples were stored and immediately frozen in 250 mL Nalgene bottles. Before chemical analyses and NIRS scans, the dry solid manure samples were run through an electric laboratory chopper (Hobart Manufacturing Co., Troy, Ohio) and mixed, and the liquid manure samples were mixed by an electric blender.

For all samples, two subsamples were taken. One was transferred to an 8 × 15 cm, 6 mil Ziploc bag for NIR scan, and the other was stored in a new Ziploc bag (dry solid samples) or transferred back to the 250 mL Nalgene bottle (liquid samples) for wet chemistry analyses. Chemical analyses for TS, VS, TN, NH₃-N, Ca, P, K, S, Na, Zn, and Cu of the samples were performed at Iowa Testing Laboratories, Inc. (Eagle Grove, Iowa). The duplicate reproducibility of laboratory nutrient analysis expressed as relative standard deviation ranged from 0.5% to 5.0%. The concentrations of TS and VS were measured according to Official Method 942.05 (AOAC, 1980). The concentrations of TN and NH₃-N of manure samples were determined by combustion analysis following *Standard Methods for the Examination of Water and Wastewater*. The concentrations of P, K, Ca, S, Na, Zn, and Cu were done with acid digestion followed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. All assay values except VS were computed on an as-is basis. The concentration of VS was expressed on the dry-weight basis.

NEAR-INFRARED SPECTROSCOPY ANALYSIS

All NIRS measurements were made with a Foss NIRSystems spectrophotometer (model 6500, Foss NIR Systems, Inc., Laurel, Md.). This instrument contains a computer-based system with a scanning monochromator equipped with Si (400-1098 nm) and PbS (1100-2498 nm) detectors. The monochromator scans the range between 400 and 2498 nm in a transmittance mode (including the visual region). The range of wavelength used for analyses was set to 1100-2500 nm on the basis of results by Reeves (2001). Spectral data were recorded at 2 nm intervals as $\log(1/R)$, where R represented decimal fraction transmittance. Groups of 20 to 25 samples were thawed to room temperature and scanned for each run. Samples were scanned using the sample transport module of the spectrophotometer to hold samples that were sealed in 8 × 15 cm, 6 mil Ziploc bags. Samples were gently

pressed onto the crystal surface to ensure good contact. Duplicate scans of each sample were examined visually for consistency.

CALIBRATION DEVELOPMENT AND DATA ANALYSIS

Software

All computations were performed with Matlab version 6.0 (MathWorks, Inc., Natick, Mass.), PLS-Toolbox version 2.01 with Matlab (Wise and Gallagher, 1998), and WinISI II 1.04. The algorithms for mathematical data pretreatments, partial least squares (PLS) regression with one-out cross-validation, and outlier detection functions were programmed in the Matlab language. One-out cross-validation means that one record is left out of the build data and only the omitted subset is used to build the prediction model. The file conversion program in the WinISI software was used to transfer data from spectra format to ASCII format so that mathematical data pretreatments and calibration developments could be performed in the Matlab environment. After the acquisition of spectral data and chemical reference values, PLS regression algorithms were used to establish mathematical relations (i.e., calibration models) between chemical reference values and spectral data for each component being measured. The optimum number of PLS factors used for constituents prediction were determined by cross-validation (Martens and Naes, 1989).

Outliers

Sample outliers, including spectral and compositional outliers, were deleted for calibrations. Spectral outliers were eliminated by principal component analysis (PCA), which identified both suspect and influential samples on the score plot of the first two principal components. After spectral outliers were removed, three data pretreatments were applied to that data set to find common compositional outliers. Common compositional outliers were defined based on the criterion that the predicted-actual difference for the sample was three standard deviations from the mean difference for all three pretreatments during calibration. Nutrients values of these outlier samples were also three standard deviations from mean values of the laboratory tests.

Mathematical Data Pretreatments

After outliers were removed, six mathematical data pretreatments (standard normal variate transformation, first and second derivatives, centering data, multiplicative scatter correction, and orthogonal signal correction) were tested to select the best data pretreatment for each constituent of each manure. The best data pretreatment was selected based on the minimum standard error of prediction (SEP). In order to test whether a single pretreatment could be selected to use for all the manures for all constituents, analysis of variance (ANOVA) was used to test pretreatment differences for each of constituents in specific manures.

Calibration Statistics

The "best" calibration equations were selected on the basis of the smallest SEP and the largest coefficient of determination (R^2) of cross-validation. To assess the predictive ability of the calibration equations, the ratio of SD to SEP (abbreviated as RPD) was used in this study. The data analytical procedure is shown in figure 1.

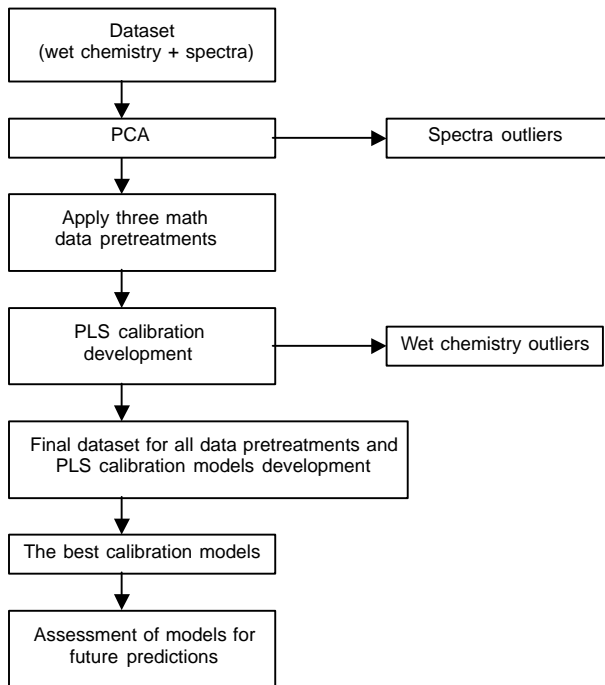


Figure 1. Flowchart of the data analytical procedure.

RESULTS AND DISCUSSION

SAMPLE COMPOSITION

The results in tables 1 through 6 show the nutrient contents of the entire samples used for calibration development. The nutrient contents of the final samples after outliers were removed were similar to those in the entire data set (data not shown). As can be seen, the composition of the samples was diverse. Therefore, a wide range of samples was used to test the feasibility of developing NIR calibrations of manure analysis.

REPEATABILITY OF SCANS

Figure 2 shows the spectra of poultry manure samples with minimum, average, and maximum TS concentrations. It illustrates that absorbance peaks of spectra occur at the same wavelengths (1730 and 2312 nm) but with different relative magnitudes. For samples with lower TS concentrations, the relative magnitudes of the peaks are more pronounced, while the absolute values are lower, which agrees with the findings of Millmier et al. (2000).

MATHEMATICAL TREATMENT FOR NIR SPECTRA

Tables 1 through 6 list the best mathematical data pretreatment for each constituent of each manure. As shown,

Table 1. Calibration and validation statistics of 111 poultry layer manure samples.

Constituent ^[a]	Wet Chemistry Statistics				Data Pretreatment ^[c]	No. of PLS Factor	Outliers Removed (%)	NIR Performance Data ^[d]			Future Predictions
	Mean	Min.	Max.	SD ^[b]				SEP	R ²	RPD	
TS (%)	66.56	26.49	88.49	19.11	SNV	9	3.6	2.28	0.97	8.38	Yes
VS (%)	60.60	27.76	79.60	10.16	1st	6	7.2	2.74	0.83	3.71	Yes
TN (%)	2.61	0.46	4.86	1.12	2nd	8	3.6	0.23	0.92	4.87	Yes
NH ₃ -N(%)	0.44	0.14	0.95	0.16	2nd	10	3.6	0.026	0.91	6.23	Yes
Ca (%)	8.94	1.47	14.86	2.97	MSC	10	5.4	1.32	0.75	2.25	No
P (%)	1.65	0.64	2.95	0.58	2nd	10	5.4	0.24	0.76	2.42	No
K (%)	1.96	0.71	3.15	0.53	1st	8	6.3	0.24	0.71	2.23	No
S (%)	0.44	0.16	0.79	0.12	2nd	6	7.2	0.058	0.70	2.15	No
Na (%)	0.38	0.11	0.76	0.12	SNV	10	7.2	0.056	0.71	2.16	No
Zn (ppm)	421.26	149.00	877.00	171.01	2nd	10	6.3	60.8	0.81	2.81	Yes
Cu (ppm)	45.60	11.00	120.00	21.81	1st	11	6.3	8.62	0.71	2.53	No

^[a] The concentration of constituents is based on % or ppm of wet-weight, except for VS, which is based on % of dry-weight.

^[b] SD = standard deviation.

^[c] 1st = first derivative, 2nd = second derivative, MSC = multiple scatter correction, and SNV = standard normal variate transformation.

^[d] Based on one-out cross-validation.

Table 2. Calibration and validation statistics of 95 poultry broiler litter manure samples.

Constituent ^[a]	Wet Chemistry Statistics				Data Pretreatment ^[c]	No. of PLS Factor	Outliers Removed (%)	NIR Performance Data ^[d]			Future Predictions
	Mean	Min.	Max.	SD ^[b]				SEP	R ²	RPD	
TS (%)	69.05	51.29	88.93	6.34	1st	10	5.3	1.45	0.91	4.37	Yes
VS (%)	73.47	50.56	89.91	7.02	2nd	10	5.3	1.98	0.86	3.54	Yes
TN (%)	2.67	1.40	4.22	0.43	2nd	9	7.4	0.13	0.80	3.32	Yes
NH ₃ -N(%)	0.51	0.28	0.88	0.12	1st	9	7.4	0.031	0.89	3.92	Yes
Ca (%)	2.02	1.22	2.74	0.33	1st	7	4.2	0.21	0.54	1.56	No
P (%)	1.49	0.98	2.81	0.22	OSC	7	4.2	0.13	0.50	1.70	No
K (%)	2.10	1.11	2.71	0.23	SNV	7	9.5	0.12	0.68	1.91	No
S (%)	0.50	0.21	0.89	0.09	CEN	10	10.5	0.04	0.66	2.19	No
Na (%)	0.65	0.33	1.09	0.10	SNV	10	7.4	0.05	0.63	2.09	No
Zn (ppm)	327.08	127.00	500.00	79.88	MSC	9	9.5	25.31	0.78	3.16	Yes
Cu (ppm)	497.20	134.00	770.00	118.75	SNV	8	9.5	66.54	0.62	1.78	No

^[a] The concentration of constituents is based on % or ppm of wet-weight, except for VS, which is based on % of dry-weight.

^[b] SD = standard deviation.

^[c] 1st = first derivative, 2nd = second derivative, CEN = centering data, MSC = multiple scatter correction, OSC = orthogonal signal correction, and SNV = standard normal variate transformation.

^[d] Based on one-out cross-validation.

Table 3. Calibration and validation statistics of 39 swine solid hoop manure samples.

Constituent ^[a]	Wet Chemistry Statistics				Data Pretreatment ^[c]	No. of PLS Factor	Outliers Removed (%)	NIR Performance Data ^[d]			Future Predictions
	Mean	Min.	Max.	SD ^[b]				SEP	R ²	RPD	
TS (%)	42.63	27.94	80.79	12.35	SNV	4	12.8	2.39	0.91	5.17	Yes
VS (%)	71.68	46.49	99.06	9.34	SNV	9	15.4	1.99	0.91	4.69	Yes
TN (%)	0.92	0.54	1.55	0.26	CEN	9	15.4	0.07	0.87	3.73	Yes
NH ₃ -N(%)	0.33	0.02	0.72	0.22	1st	6	12.8	0.04	0.92	5.39	Yes
Ca (%)	1.31	0.41	8.42	1.36	1st	9	10.3	0.21	0.94	6.47	Yes
P (%)	0.63	0.23	1.59	0.29	1st	3	15.4	0.13	0.74	2.21	No
K (%)	1.25	0.55	2.30	0.42	SNV	9	10.3	0.09	0.90	4.67	Yes
S (%)	0.31	0.17	0.66	0.11	2nd	6	7.7	0.056	0.70	1.93	No
Na (%)	0.26	0.12	0.45	0.08	1st	10	17.9	0.03	0.80	2.54	No
Zn (ppm)	167.85	46.00	386.00	79.45	CEN	7	10.3	30.98	0.81	2.56	No
Cu (ppm)	29.36	10.00	51.00	10.90	CEN	8	15.4	4.01	0.82	2.72	No

^[a] The concentration of constituents is based on % or ppm of wet-weight, except for VS, which is based on % of dry-weight.

^[b] SD = standard deviation.

^[c] 1st = first derivative, 2nd = second derivative, CEN = centering data, and SNV = standard normal variate transformation.

^[d] Based on one-out cross-validation.

Table 4. Calibration and validation statistics of 72 beef cattle manure samples.

Constituent ^[a]	Wet Chemistry Statistics				Data Pretreatment ^[c]	No. of PLS Factor	Outliers Removed (%)	NIR Performance Data ^[d]			Future Predictions
	Mean	Min.	Max.	SD ^[b]				SEP	R ²	RPD	
TS (%)	72.47	33.93	92.93	15.47	2nd	9	5.6	2.98	0.90	5.19	Yes
VS (%)	42.84	11.08	75.79	16.69	2nd	7	6.9	3.29	0.91	5.07	Yes
TN (%)	1.18	0.27	2.18	0.47	2nd	8	9.7	0.11	0.88	4.28	Yes
NH ₃ -N(%)	0.16	0.01	0.37	0.10	SNV	10	6.9	0.02	0.89	4.86	Yes
Ca (%)	3.81	1.13	8.88	1.63	MSC	9	9.7	0.66	0.72	2.48	No
P (%)	0.50	0.11	2.59	0.29	2nd	10	5.6	0.07	0.91	4.09	Yes
K (%)	1.04	0.19	2.30	0.50	OSC	10	2.8	0.14	0.87	3.57	Yes
S (%)	0.32	0.08	0.53	0.09	SNV	8	5.6	0.04	0.78	2.31	No
Na (%)	0.24	0.05	0.45	0.12	OSC	10	8.3	0.03	0.90	4.14	Yes
Zn (ppm)	165.83	63.00	329.00	63.86	1st	7	8.3	34.7	0.66	1.84	No
Cu (ppm)	34.21	9.00	59.00	12.58	1st	9	6.9	6.58	0.71	1.91	No

^[a] The concentration of constituents is based on % or ppm of wet-weight, except for VS, which is based on % of dry-weight.

^[b] SD = standard deviation.

^[c] 1st = first derivative, 2nd = second derivative, MSC = multiple scatter correction, OSC = orthogonal signal correction, and SNV = standard normal variate transformation.

^[d] Based on one-out cross-validation.

Table 5. Calibration and validation statistics of 88 swine liquid lagoon manure samples.

Constituent ^[a]	Wet Chemistry Statistics				Data Pretreatment ^[c]	No. of PLS Factor	Outliers Removed (%)	NIR Performance Data ^[d]			Future Predictions
	Mean	Min.	Max.	SD ^[b]				SEP	R ²	RPD	
TS (%)	0.57	0.16	3.08	0.38	2nd	8	3.4	0.07	0.92	5.47	Yes
VS (%)	36.33	27.62	75.33	7.48	1st	10	6.8	1.81	0.88	4.13	Yes
TN (%)	0.069	0.010	0.290	0.042	2nd	8	9.1	0.012	0.83	3.49	Yes
NH ₃ -N(%)	0.092	0.005	0.205	0.038	2nd	9	5.7	0.01	0.88	3.75	Yes
Ca (%)	0.007	0.003	0.071	0.008	2nd	10	3.4	0.002	0.90	4.22	Yes
P (%)	0.015	0.003	0.077	0.010	2nd	8	3.4	0.002	0.91	4.85	Yes
K (%)	0.132	0.043	0.253	0.055	OSC	6	2.3	0.025	0.73	2.19	No
S (%)	0.003	0.001	0.029	0.003	2nd	7	1.1	0.001	0.83	3.36	Yes
Na (%)	0.03	0.01	0.05	0.01	1st	9	3.4	0.003	0.80	2.63	No
Zn (ppm)	3.06	0.90	30.00	3.61	OSC	8	2.3	1.38	0.79	2.61	No

^[a] The concentration of constituents is based on % or ppm of wet-weight, except for VS, which is based on % of dry-weight.

^[b] SD = standard deviation.

^[c] 1st = first derivative, 2nd = second derivative, and OSC = orthogonal signal correction.

^[d] Based on one-out cross-validation.

the best mathematical data treatment for different constituents in the same manure or the same constituent for different manures may be different. Further, in almost all cases, the best mathematical data treatment is significantly different from the second best mathematical data treatment for each constituent of each manure ($P < 0.05$). Therefore, the choice

of data pretreatment will depend on a specific constituent of manure. Results of this study provide the basis for the future data pretreatment for a specific constituent in manure samples. Applying the best data pretreatment for each constituent in this study could increase the prediction ability of calibration models and optimize the calibration accuracy.

Table 6. Calibration and validation statistics of swine slurry manure.

Constituent ^[a]	Wet Chemistry Statistics				Data Pretreatment ^[c]	No. of PLS Factor	Outliers Removed (%)	NIR Performance Data ^[d]			Future Predictions
	Mean	Min.	Max.	SD ^[b]				SEP	R ²	RPD	
TS (%)	6.04	1.07	16.08	3.29	SNV	8	9.4	0.68	0.92	4.84	Yes
VS (%)	71.69	56.92	87.80	5.54	SNV	8	8.2	1.39	0.87	3.98	Yes
TN (%)	0.349	0.040	0.540	0.096	CEN	10	5.9	0.021	0.91	4.58	Yes
NH ₃ -N(%)	0.273	0.032	0.406	0.063	2nd	10	4.7	0.014	0.91	4.52	Yes
Ca (%)	0.246	0.026	1.356	0.241	2nd	10	2.4	0.073	0.86	3.30	Yes
P (%)	0.240	0.017	0.678	0.151	2nd	10	5.9	0.032	0.90	4.72	Yes
K (%)	0.235	0.094	0.352	0.061	2nd	10	7.1	0.02	0.87	3.05	Yes
S (%)	0.018	0.005	0.059	0.010	1st	4	8.2	0.004	0.70	2.54	No
Na (%)	0.038	0.020	0.062	0.009	2nd	11	5.9	0.003	0.88	3.05	Yes
Zn (ppm)	68.21	7.00	191.00	35.86	MSC	10	4.7	12.84	0.83	2.79	No
Cu (ppm)	30.31	5.00	81.00	17.35	SNV	10	4.7	4.61	0.87	3.76	Yes

[a] The concentration of constituents is based on % or ppm of wet-weight, except for VS, which is based on % of dry-weight.

[b] SD = standard deviation.

[c] 1st = first derivative, 2nd = second derivative, CEN = centering data, MSC = multiple scatter correction, and SNV = standard normal variate transformation.

[d] Based on one-out cross-validation.

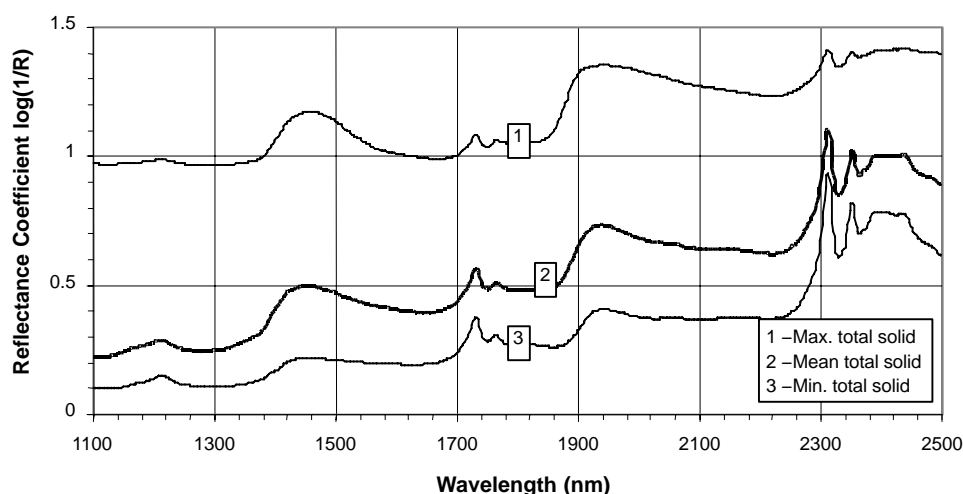


Figure 2. NIR spectra of TS minimum, average, and maximum for poultry manure sample set.

NIR CALIBRATION AND VALIDATION STATISTICS

Outliers

Samples that were predicted very poorly (concentration outliers) or that were spectrally very different from the majority of the samples (spectral outliers) were removed. Tables 1 through 6 show the percent of outliers removed for each constituent of each manure during calibrations. The percent of outlier removed in this study is less than 10%, except for solid swine hoop manure with a small sample size, which is consistent with the range of previous reports (Millmier et al., 2000; Reeves and Van Kessel, 2000; Reeves, 2001).

Determinations of Total and Volatile Solids and Total and Ammonia Nitrogen

The calibration and validation statistics for poultry solid layer, poultry broiler litter, swine solid hoop, beef cattle, swine liquid lagoon, and swine slurry manure samples are shown in tables 1 through 6, respectively. The R² values of the one-out cross-validation for TS, TN, and NH₃-N are between 0.80 and 0.97 for all manure samples. Although it is difficult to make direct comparison with other results due to the variable nature of manure, in general, the R² values of this study are similar to those reported in previous reports (Asai

et al., 1993; Reeves and Van Kessel, 2000; Reeves, 2001). The results of the one-out cross-validation for TS, VS, TN, and NH₃-N are also shown in figures 3 through 6. Results indicate that NIRS is able to accurately determine TS, VS, TN, and NH₃-N for all manures.

Determinations of Minerals

The R² values of the one-out cross-validation for minerals ranged from 0.70 to 0.81, 0.50 to 0.78, 0.74 to 0.94, 0.66 to 0.91, 0.73 to 0.91, and 0.70 to 0.90 in poultry solid layer, poultry broiler litter, swine solid hoop, beef cattle, swine liquid lagoon, and swine slurry manure samples, respectively. Reeves and Van Kessel (2000) reported that the R² values of the one-out cross-validation for K and P were 0.569 and 0.342, respectively, based on 107 dairy manure samples before eight outliers were removed. Reeves (2001) reported that the R² values of calibrations for minerals were between 0.401 and 0.8 based on 207 poultry manure samples before outliers were removed. He also pointed out that removal of outliers did not produce a very satisfactory calibration for minerals. Although the calibrations developed for minerals in this study are better than those in other studies (Millmier et al., 2000; Reeves and Van Kessel, 2000; Reeves, 2001), it seems that the calibrations are still not adequate for most

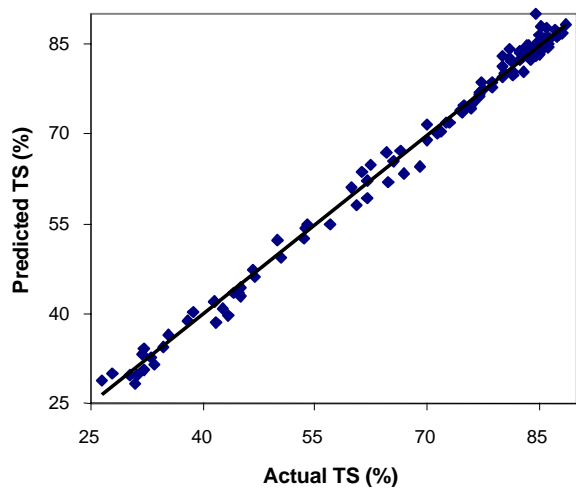


Figure 3. Predicted versus actual from one-out cross-validation for total solids (TS) in poultry solid layer manure.

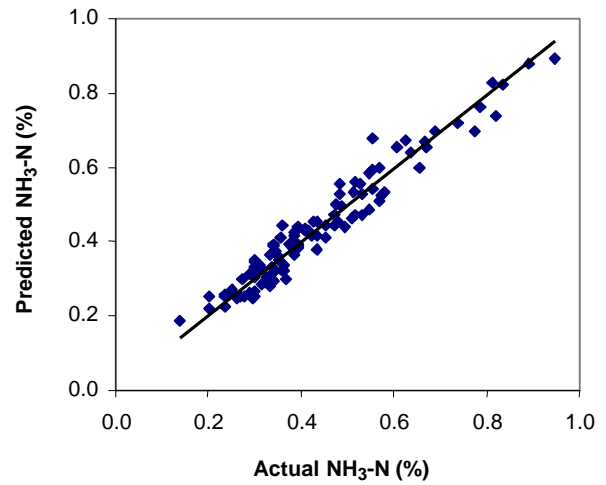


Figure 6. Predicted versus actual from one-out cross-validation of for ammonia nitrogen (NH₃-N) in poultry solid layer manure.

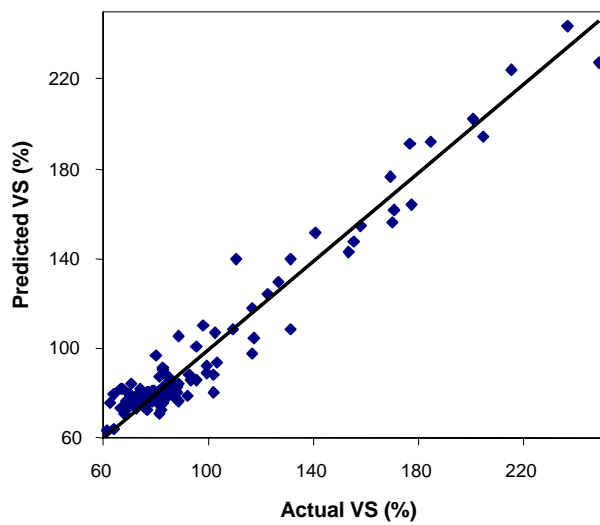


Figure 4. Predicted versus actual from one-out cross-validation for volatile solid (VS) in beef cattle feedlot manure.

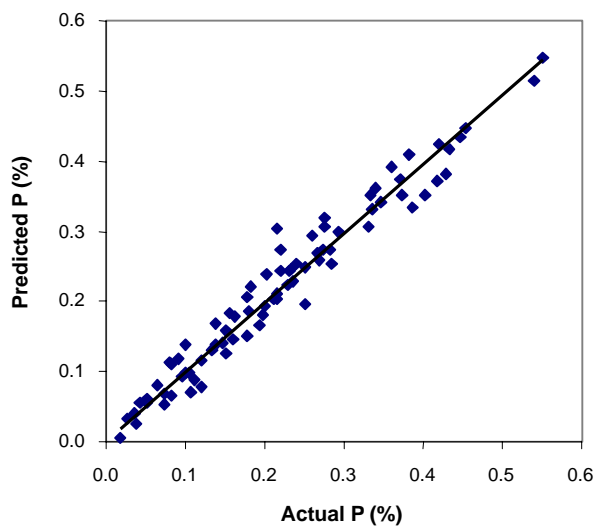


Figure 7. Predicted versus actual from one-out cross-validation of for phosphorus (P) in swine slurry manure.

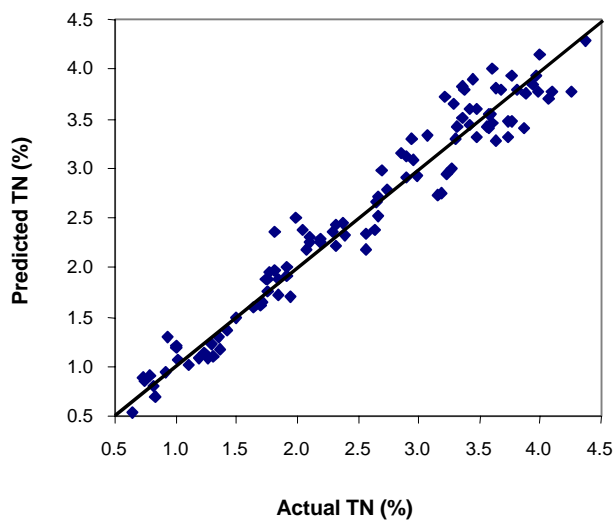


Figure 5. Predicted versus actual from one-out cross-validation of for total nitrogen (TN) in poultry solid layer manure.

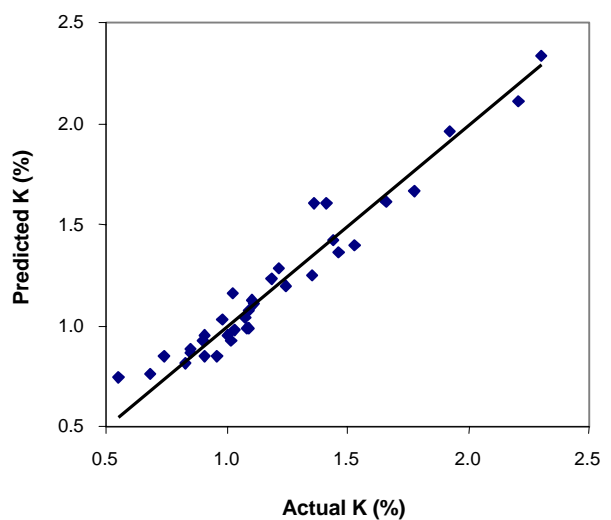


Figure 8. Predicted versus actual from one-out cross-validation of for potassium (K) in swine solid manure.

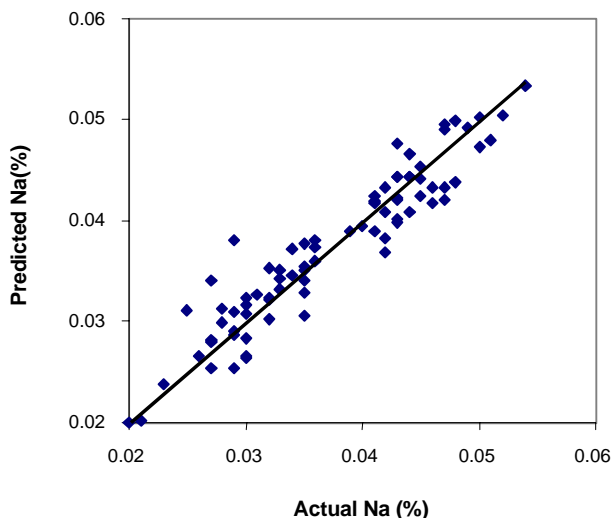


Figure 9. Predicted versus actual from one-out cross-validation of for sodium (Na) in swine slurry manure.

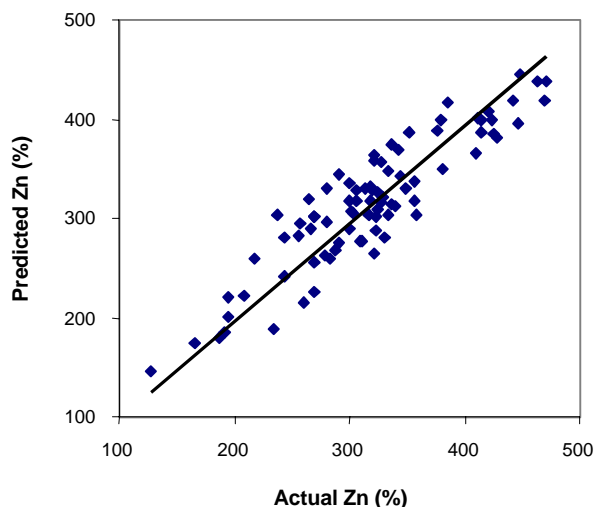


Figure 10. Predicted versus actual from one-out cross-validation of for zinc (Zn) in poultry solid broiler litter manure.

minerals in manure samples. However, based on the RPD values shown in tables 1 through 6, it is possible to use NIRS to analyze selected minerals in certain manures, for example, P in beef cattle, swine liquid lagoon, and swine slurry manure samples. The results of the one-out cross-validation for P, K, Na, and Zn, which could be determined by NIRS, are shown in figures 7 through 10.

Although the accuracy of calibrations for minerals depends on relationships between organic components and the minerals (Clark et al., 1985; Shenk et al., 1992), it is still possible to determine some minerals by using those relationships as seen in this study. The data pretreatment used in this study could increase the predictive ability of using NIRS to determine the minerals in manure samples. In general, results of this study indicate that using NIRS to determine minerals in manure samples is limited, but possible for certain minerals.

PREDICTION OF NUTRIENT CONTENTS

A small SEP alone does not clearly reflect the usefulness of an NIRS calibration for manure evaluation. If the ratio of

the standard deviation (SD) of the constituent in the sample population to the SEP (RPD) is calculated, it helps in determining whether NIRS is useful for analyzing the manure. If the RPD is high, then NIRS predictions can divide the samples into subgroups of low, medium, and high contents of the selected constituent. Tables 1 through 6 show the RPD for all constituents involved in this study. If the ratio exceeds a value of 3, the calibration equation can predict the constituent. Otherwise, the ability of the calibration equation is limited (Fontaine et al., 2001). These cutoff values for RPDs are based literature values used in other industries (Malley et al., 1999, 2002; Fontaine et al., 2001). Acceptable values have not been established for manure samples.

Tables 1 through 6 show that NIRS can predict TS, VS, TN, and $\text{NH}_3\text{-N}$ well in all manures, which agrees with the findings of Millmier et al. (2000), Reeves and Van Kessel (2000), and Reeves (2001). Tables 1 through 6 also show that NIRS can predict several minerals in certain manure samples, for example, P in beef cattle, swine lagoon, and swine slurry manure samples, which disagrees with the findings of Reeves and Van Kessel (2000) and Reeves (2001), who reported that NIRS is not suitable for the determination of minerals in manure samples. These results are also not consistent with the findings of Millmier et al. (2000), who reported that NIRS could not be used for quick determination of P in beef cattle, swine liquid lagoon, and swine slurry manure samples using the ratio of range:SEP. Using different criterion (range:SEP versus SD/SEP) may lead to different conclusions. RPD, as used in this study, is a meaningful measure of NIRS prediction because the RPD value not only reflects SEP but also highly coincides with the R^2 value (tables 1 through 6). Using the RPD value to determine whether an NIRS calibration can be used for future prediction has been applied to soils and feeds (Malley et al., 1999, 2002; Fontaine et al., 2001) but has not been applied to manure samples. The main difference between this study and previous studies is the use of pretreatments. Clearly, pretreatment of the raw data is beneficial in adapting NIRS to predicting manure nutrients. However, the fact that the choice of data pretreatment will depend on a specific constituent of manure might limit the use of data pretreatment in NIRS application.

CONCLUSIONS

This study showed that by utilizing selected data pretreatments, NIRS is a potentially usable method to determine manure nutrient and solids concentrations, including some minerals, in liquid and solid forms of manure. However, the application of NIR spectroscopy to livestock manure samples has been limited by the requirement that each instrument must be individually calibrated. Although it is not difficult to operate the calibration software, extensive training and experience and accurate chemical analysis of the calibration samples are required to develop a comprehensive and accurate analysis equation for each constituent. One possible solution to the problem is the transfer of NIR calibrations from one instrument to another such that only one calibration laboratory would be required.

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REFERENCES

- AOAC. 1980. *Official Methods of Analysis*. 13th ed. Washington, D.C.: Association of Official Analytical Chemists.
- Asai, T., S. Shimizu, T. Koga, and M. Sato. 1993. Quick determination of total nitrogen, total carbon, and crude ash in cattle manure using near-infrared reflectance spectroscopy. *Nippon Dojo Hiryogaku Zasshi* 64(6): 669-675.
- Clark, D. H. 1985. Other forage and feed nutrients. In *Near-Infrared Reflectance Spectroscopy (NIRS): Analysis of Forage Quality*, 58. G. C. Marten, J. S. Shenk, and F. E. Barton II, eds. USDA Handbook 643. Washington, D.C.: USDA Agricultural Research Service.
- Fontaine, J., J. Horr, and B. Schirmer. 2001. Near-infrared reflectance spectroscopy enables the fast and accurate prediction of the essential amino acid contents in soy, rapeseed meal, sunflower meal, peas, fish meal, meat meal products, and poultry meal. *J. Agric. Food Chem.* 49(1): 57-66.
- Leco. 1999. Conditioning fields scientifically. St. Joseph, Mich.: Leco Corporation. Available at: www.leco.org/whatsnew/recentarticles.
- Li, W., G. Pierre, and M. Marc. 1996. Quantitative analysis of individual sugars and acids in orange juices by near-infrared spectroscopy of dry extract. *J. Agric. Food Chem.* 44(8): 2252-2259.
- Lorimor, J. C., and S. W. Melvin. 1996. Nutrient losses from properly manured land. ASAE Paper No. MC96-120. St. Joseph, Mich.: ASAE.
- Malley, D. F., L. Yesmin, D. Wary, and S. Edwards. 1999. Application of near-infrared spectroscopy in analysis of soil mineral nutrients. *Comm. Soil Science and Plant Analysis* 30(7/8): 999-1012.
- Malley, D. F., L. Yesmin, and R. G. Eilers. 2002. Rapid analysis of hog manure and manure-amended soils using near-infrared spectroscopy. *SSSA J.* 66(5): 1677-1686.
- Martens, H., and T. Naes. 1989. Assessment, validation, and choice of calibration method. In *Multivariate Calibration*, 237-266. New York, N.Y.: Wiley.
- Millmier, A., J. Lorimor, C. Hurburgh Jr., C. Fulhage, J. Hattey, and H. Zhang. 2000. Near-infrared sensing of manure nutrients. *Trans. ASAE* 43(4): 903-908.
- Nakatani, M., Y. Harada, K. Haga, and T. Osada. 1996. Near infrared spectroscopy analysis of the changes in quality of cattle wastes during composting processes. *J. Japanese Soil and Fertil. Soc.* 66(2): 159-161.
- Prantner, S. R., R. S. Kanwar, J. C. Lorimor, and C. H. Pederson. 1999. Management of swine manure through the use of soil infiltration and wetland systems. ASAE Paper No. MC99-116. St. Joseph, Mich.: ASAE.
- Reeves, J. B., III. 2001. Near-infrared diffuse reflectance spectroscopy for the analysis of poultry manures. *J. Agric. Food Chem.* 49(5): 2193-2197.
- Reeves, J. B., III., and J. S. Van Kessel. 2000. Near-infrared spectroscopic determination of carbon, total nitrogen, and ammonium-N in dairy manures. *J. Dairy Sci.* 83(8): 1829-1836.
- Shenk, J. S., J. J. Workman, and M. O. Westerhaus. 1992. Application of NIR spectroscopy to agricultural products. In *Handbook of Near-Infrared Analysis*, 383-431. D. A. Burns and E. W. Ciurczak, eds. New York, N.Y.: Marcel Dekker.
- Van Kessel, J. S., R. B. Thompson, and J. B. Reeves III. 1999. Rapid on-farm analysis of manure nutrient using quick tests. *J. Prod. Agric.* 12(2): 215-224.
- Van Kessel, J. S., and J. B. Reeves III. 2000. On-farm quick tests for estimating nitrogen in dairy manure. *J. Dairy Sci.* 83(8): 1837-1844.
- Warnemuende, E. A., J. L. Baker, R. S. Kanwar, J. C. Lorimor, S. Mickelson, and S. W. Melvin. 1999. The effects of swine manure application systems on surface and groundwater quality. ASAE Paper No. 992197. St. Joseph, Mich.: ASAE.
- Wise, B. M., and N. B. Gallagher. 1998. PLS_Toolbox Version 2.01 for use with Matlab. Manson, Wash.: Eigenvector Research.