Measurement of nutrients in Saskatchewan hog manures using near-infrared spectroscopy

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Dagnew, M.D., Crowe, T.G. and Schoenau, J.J. 2004. **Measurement of nutrients in Saskatchewan hog manures using near-infrared spectroscopy.** Canadian Biosystems Engineering/Le génie des biosystèmes au Canada **46**: 6.33-6.37. The objective of this study was to use near-infrared spectroscopy (NIRS) to predict nutrient concentrations and physical parameters of hog manure from 13 Saskatchewan farms and producer submissions to a commercial laboratory. Nutrients predicted were total Kjeldhal nitrogen (TKN), total phosphorus (P), and potassium (K). Total solids (TS) were also measured. Multiple linear regression (MLR) was used to develop calibration models using a calibration set of 63 samples. Performance of the calibration models was evaluated using a validation set of 25 samples. The performance of the models was quantified by determining the coefficient of determination (r^2), the ratio of the standard deviation of the reference chemistry values to the standard error of prediction (RPD), and the ratio of the range of reference chemistry values to the standard error of prediction (RER). Total Kjeldhal nitrogen (r^2 =0.89, RPD = 2.29, and RER = 10.22) and TS (r^2 = 0.92, RPD = 3.63, and RER = 17.04) were predicted successfully, while models predicting P (r^2 = 0.79, RPD = 1.92, and RER = 6.33) and K (r^2 = 0.68, RPD = 1.14, and RER = 6.00) were less accurate. **Keywords**: near-infrared reflectance spectroscopy, NIRS, manure management, multiple linear regression, MLR.

L'objectif de cette étude était d'utiliser la spectroscopie aux infrarouges rapprochés (SIRR) pour prédire les concentrations en éléments fertilisants et les paramètres physiques de lisier de porcs provenant de 13 fermes de la Saskatchewan et d'échantillons de producteurs soumis à un laboratoire commercial. Les éléments fertilisants considérés étaient l'azote total Kjedhal (TKN), le phosphore total (P) et le potassium (K). Les solides totaux (ST) ont aussi été mesurés. La régression multiple linéaire (RML) a été utilisée pour développer des modèles d'étalonnage en utilisant un ensemble de 63 échantillons. La performance des modèles était évaluée en déterminant le coefficient de détermination (r^2), le rapport entre la déviation standard des valeurs chimiques de référence et l'erreur standard de prédiction (RPD) ainsi que le rapport entre la plage des valeurs chimiques de référence et l'erreur standard de prédiction (RER). L'azote total Kjedhal (r^2 =0,89, RPD = 2,29, et RER = 10,22) et les solides totaux (r^2 = 0,92, RPD = 3,63, et RER = 17,04) ont été prédits correctement par les modèles alors que les modèles prédisant P (r^2 = 0,79, RPD = 1,92, et RER = 6,33) et K (r^2 = 0,68, RPD = 1,14, et RER = 6,00) se sont avérés moins précis. **Mots clés**: spectroscopie aux infrarouges rapprochés, SIRR, gestion du lisier, régression linéaire multiple, RLM.

INTRODUCTION

The hog population in Saskatchewan increased from 1.2 to 1.8 million between 1996 and 2000 and is expected to increase to 5 million by 2005 (Prairie Swine Centre 2000). Each weanling pig produces 1.6 L of liquid manure per day, while a nursing sow and her offspring can produce 22 L per day. As a general rule of thumb, it is expected that farrow-to-finish hog operations will produce 70 L of manure per sow per day (Prairie Swine Centre 2000). As the livestock industry continues to expand, one of the major issues facing livestock producers is how to handle manure produced on their farms.

The practice of using manure as a crop fertilizer can be ecologically sound provided precautions are taken to avoid risk of soil over-fertilization and contamination of surface and/or groundwater through runoff or leaching. To reduce these risks, it is necessary to quantify the nutrients present in the manure prior to land application. The research conducted for this paper used NIRS to determine these nutrients.

Malley et al. (2002) conducted two experiments that used NIRS in the 400-2500 nm region to measure physical parameters and nutrient concentrations in hog manure. Calibration models were developed using MLR and first and second order derivatives were used for data smoothing. In the first study of seven sites, several forms of N and several forms of P were measured successfully, while K was measured with less success. In the second study of 25 sites, measurements of N and P were less successful compared to the first study. Moisture content was predicted successfully in this experiment, and the difference was attributed to the greater variability in the samples of the second study, representing 25 effluent ponds compared to seven effluent ponds in the first study.

Millimier et al. (2000) used NIRS to measure physical parameters and nutrients in hog manure (from pits and lagoons) and solid beef feedlot manure. Calibration equations were developed using partial least squares (PLS) regression, and principal component analysis was used to remove outliers. For all three types of manure, several forms of N (including TKN) and K were predicted successfully, while P was not.

Ye et al. (2001) used NIRS to measure the concentration of nutrients and minerals in chicken manure using wavelengths in the 1100-2500 nm region. Raw spectral data were treated with multiplicative scatter correction (MSC) and models were developed using PLS regression. Several forms of N (including TKN) and TS were measured successfully. However, it was determined that some minerals (K) cannot be measured using NIRS, while others (P) required additional methods of spectral standardization to improve the precision of calibration equations.

Reeves (2001) used NIRS to determine nutrient and mineral concentration in poultry manures. In this research, PLS

Table 1. Chemical composition of manure in the calibration and validation sets.

Constituents	Calibration set (63 samples)		Validation set (25 samples)	
	Range	SD	Range	SD
TKN (mg/g)	1.77 - 12.45	2.55	1.81 - 11.83	2.24
T (mg/g)	0.04 - 2.71	0.87	0.04 - 2.70	0.81
K (mg/g)	0.10 - 3.22	0.67	0.11 - 3.11	0.57
TS (%)	0.80 - 15.75	4.05	0.90 - 14.53	2.90

regression was used to develop calibration models and spectral data were treated using either MSC or mean and variance scaling. Results from this study indicated that several forms of N were predicted successfully and NIRS was not suitable for measuring P and K.

OBJECTIVES

The objective of this study was to use NIRS to determine nutrient concentrations and physical characteristics of liquid swine manure from Saskatchewan hog farms. Multiple linear regression was used to develop calibration models for predicting TKN, P, K, and TS in liquid swine manure. Further, the predictive ability of these linear regression models was evaluated.

MATERIALS and METHODS

Samples

Eighty-eight swine manure samples were collected from 13 Saskatchewan hog farms and from producer submissions to a commercial laboratory (Enviro-Test Lab, Saskatoon, SK). Hog farms included in the study were located near Beechy, Burr, Dixon, Englefeld, Lanigan, Leroy, Loon Lake, Perdue, Plenty, Melfort, Star City, Riverhurst, and Valparaiso.

Thirty-three samples were collected in the fall of 1999 and 20 were collected in the spring of 2000. These samples were collected from the injection orifice of manure application equipment during application to research plots at the various sites. These samples were chilled immediately after collection to 4°C, transported to a laboratory at the University of Saskatchewan, and then frozen at -20°C. Reflectance measurements of this batch were performed in the winter of 2001. Samples were thawed and subjected to chemical analyses prior to reflectance measurements. A second batch (20 samples) was obtained from producer submissions to a commercial laboratory in the spring of 2001. Sample collection protocol for these samples was followed as set by the Enviro Test Laboratories (ETL) standard (ETL 2000). Chemical analyses and reflectance measurements were done simultaneously soon after collection for these samples. A third batch (15 samples) was collected from earthen manure storage units at different depths.

Chemical analysis

Wet chemistry analysis for total Kjeldhal nitrogen and total phosphorus were conducted in the Soil Science Laboratory, University of Saskatchewan. A standard H_2SO_4-H_2O_2 digestion followed by colorimetry was done for analyses of TKN and P. The same H_2SO_4-H_2O_2 extract was analyzed for potassium using inductively coupled plasma at a commercial laboratory (Western Ag Labs, Saskatoon, SK). Total solid data were acquired by air-drying samples in an oven at 40°C for 24 hours.

Spectral measurements

Diffuse reflectance spectra were recorded using a dual-beam spectrophotometer (Varian Cary 5G UV/visible/NIR, Varian Inc., Cary, NC). The spectrophotometer was operated using an integrating sphere and a dedicated sample holder consisting of black opaque delrin enveloping a standard cuvette (45 x 125 mm, path length of 10 mm with a capacity of working within the 170–2700 nm wavelength range) (Dagnew 2002). Reflectance data were recorded in 1-nm increments between 250 - 870 nm and in 2-nm increments between 870 - 2500 nm.

Samples were divided into two replicates and replicates were divided into two sub-samples. Sub-samples were scanned four times, with each scan consisting of three reflectance measurements. Sub-samples were stirred between scans to prevent solids from settling. Reflectance measurements for each sample (12 per sub-sample, 24 per replicate, 48 per sample) were averaged offline to produce an average reflectance spectrum for each sample. Reflectance values were obtained as percentages relative to a baseline obtained by scanning spectralon inside a matched cuvette. Absolute reflectance values were calculated using the absolute reflectance spectrum for the baseline material.

Data pre-processing

The spectra measured with the spectrophotometer provided reflectance values at 1435 wavelengths between 250 and 2500 nm. Data were averaged over sequential 10-nm ranges, using spreadsheet software. This reduced the size of the data vectors from 1435 elements to 227. Wavelengths where the data were noisy were eliminated prior to the development of the calibration models. Wavebands excluded were from: 2000 - 2500 nm (50 wavebands) where the spectra were noisy due to low reflectivity of the manure and lower sensitivity of the instrument, 870 nm (1 waveband) in which the reflectance levels fluctuated randomly due to noise from the detector change over point, and 250 - 400 nm (15 wavebands) where the spectra showed very little difference between the samples. Velasco and Gruneberg (1999) suggested that the spectral regions around the water absorption dips should be removed when analyzing wet materials. Thus bands at 1450 and 1900 were also eliminated. In total, 68 wavebands were eliminated from the data set.

Calibration procedure

The dataset was divided into calibration and validation sets. Seventy percent of the samples were employed as training data for developing the calibration models while the remaining 30% were used to test their performance. The calibration and validation data sets were created using the data partition node in SAS/Enterprise miner® (Enterprise miner Version 4, SAS Institute Inc., Cary, NC). Table 1 shows the ranges of chemical composition and variation of manure nutrients in the calibration and validation data sets.

Models with fewer predictors are desirable because they minimize problems that occur with over-fitting of the calibration

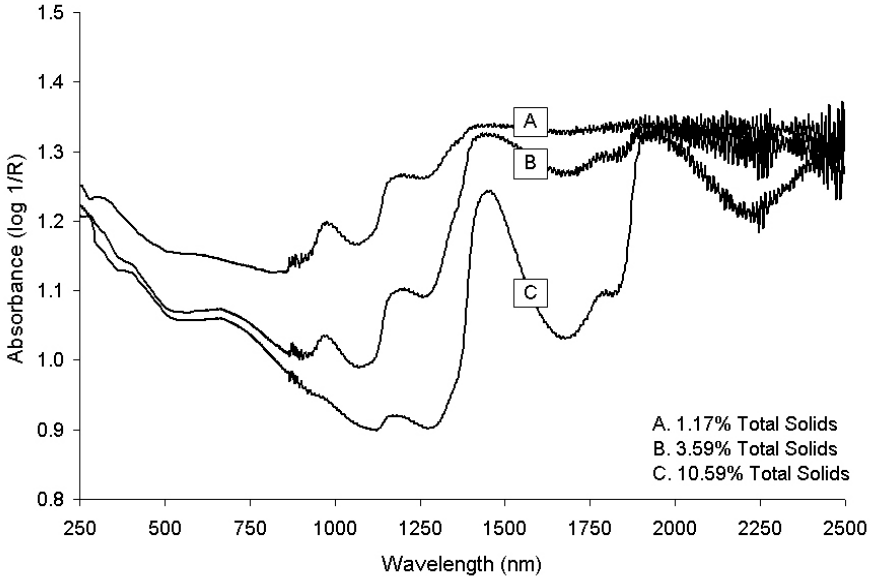

Fig. 1. Absorbance spectra of hog manure.

data set. Hruschka (1987) indicated that a simple rule of thumb is to have 5-15 samples for each predictor used in the model. With 63 samples in the calibration data set, this dictated that the number of reflectance terms in models should be 4 - 12. Five calibration equations, each containing 1 - 5 predictor variables, were developed.

Calibration equations were generated using multiple linear regression (MLR) procedures (SAS 1999). Selection of the optimum wavelengths for inclusion in calibration models was done using the REG procedure in SAS® (SAS Version 8, SAS Institute Inc., Cary, NC). The MINR option of the REG procedure was used to develop the calibration models using stepwise regression.

The best calibration models were those that had the highest coefficient of determination (r^2) between the predicted and measured values and the lowest standard error of prediction (SEP). Other statistics were determined to evaluate the performance of the calibration models. These were RER, the ratio of the range of reference chemistry values to SEP and RPD, the ratio of the standard deviation of the reference chemistry values to SEP, as defined by Williams (1987).

Values of RER in the range of 4 - 8 indicate the possibility of distinguishing between high and low chemistry values. Values of RER in the range of 8 - 12 indicate the possibility of predicting quantitative data, and RER values greater than 12 indicate good predictability (Ye et al. 2001, Millimier et al. 2000). Further, it is suggested that for the successful analysis of agricultural commodities, r^2 should be greater than 0.95, RPD should be greater than 5, and RER should be greater than 20. In more variable samples, such as manure or soil, an r^2 greater than 0.9, an RPD greater than 3, and an RER greater than 10 will indicate successful calibrations (Malley et al. 2002).

RESULTS and DISCUSSION

Visible and NIR spectral characterization

Figure 1 shows the absorbance spectra of manure samples from a site. Noise was present in the 2100-2500 nm range, due to low reflectivity of the manure and lower sensitivity of the instrument. The visible and near infrared spectra contained discernable reflectance dips and peaks which could be used to identify differences between the samples.

Spectro-chemical models

The wavelengths and regression coefficients for the best calibration models are given in Table 2. The wavelengths selected for use in the calibration models did not follow a well-defined trend, with some incorporating wavelengths at the lower end of the spectrum and others using reflectance from the entire spectrum.

Table 3 shows statistical data that indicate the performance of the calibration models during validation. Measurements of TS (r^2 = 0.92, RPD = 3.63, and RER = 17.04) and TKN (r^2 = 0.89, RPD = 2.43, and RER = 10.22) were successful. Measurements of P (r^2 = 0.79, RPD = 1.93, and RER = 6.33) and K (r^2 = 0.68, RPD = 1.14, and RER = 6.00) were less successful. Figures 2 to 5 show the final validation results for each constituent.

In a study of hog manure by Malley et al. (2002) various forms of N were measured successfully (r^2 = 0.94 – 0.98, RPD = 3.95 – 6.78, and RER = 14.22 – 22.6). In a second study of hog manure by the same authors, measurements of these forms of N were less successful (r^2 = 0.66 – 0.79, RPD = 1.71 – 2.12, and RER = 6.98 – 9.11). The difference in predictive ability between these two studies was attributed to greater variability in the second study, which had 25 sites compared to seven in the first study. Prediction of TKN in this research (13 sites) was more successful than the second study by Malley et al. (2002) and less accurate than their first study.

Table 2. Calibration model parameters developed using MLR.

Constituents	Waveband (nm)	Regression coefficients					
		b_0	b_1	b_2	b_3	b_4	b_5
TKN	1380, 1010, 540	-6.20	1.93	-0.50	0.71		
P	1720, 1690, 1230, 1040, 880	-1.21	16.39	-17.1	1.68	-1.08	0.41
K	2000, 520, 510, 480, 400	-6.36	2.66	-21.42	27.61	-5.19	-1.63
TS	1990, 1810, 1660, 1360	10.13	-9.59	22.04	-19.82	4.95	

Table 3. Performance of calibration models during validation.

Constituent	SEP	r^2	RPD	RER
TKN	0.98	0.89	2.43	10.22
P	0.42	0.79	1.93	6.33
K	0.50	0.68	1.14	6.00
TS	0.80	0.92	3.63	17.04

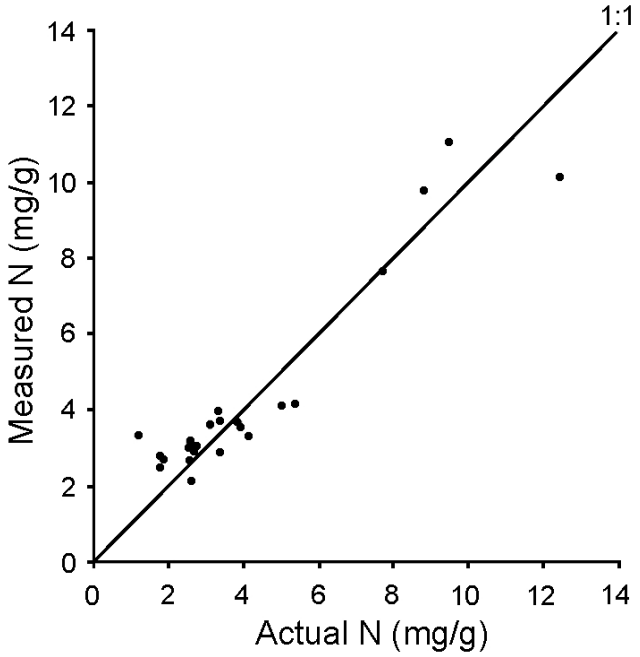

Fig. 2. Validation results for N.

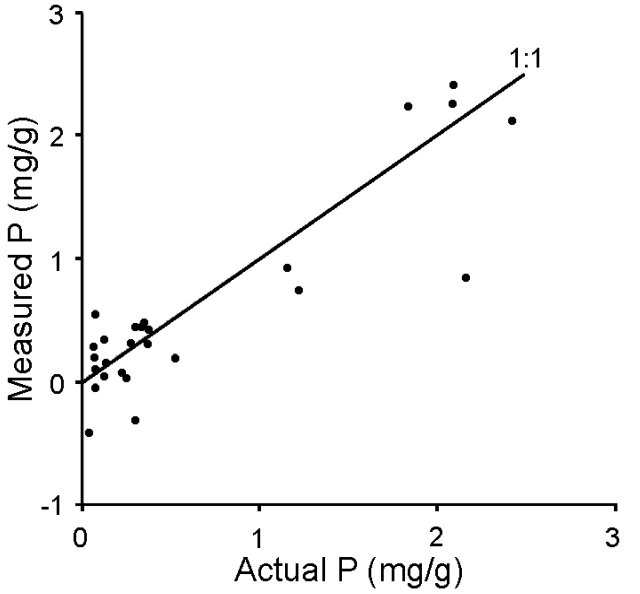

Fig. 3. Validation results for P.

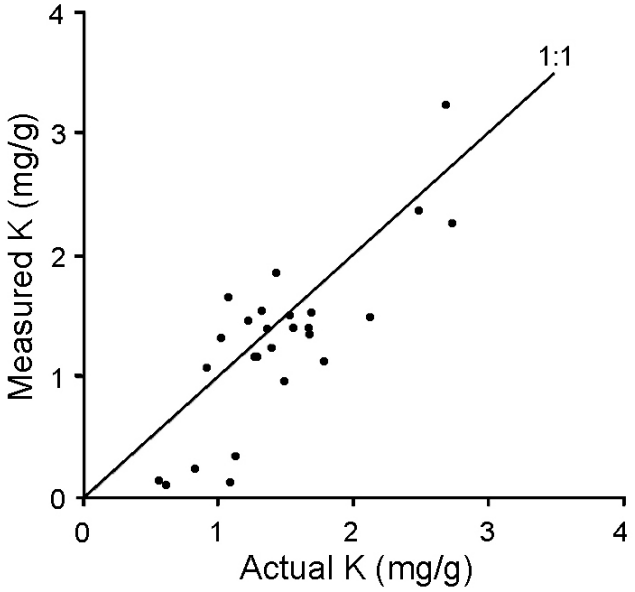

Fig. 4. Validation results for K.

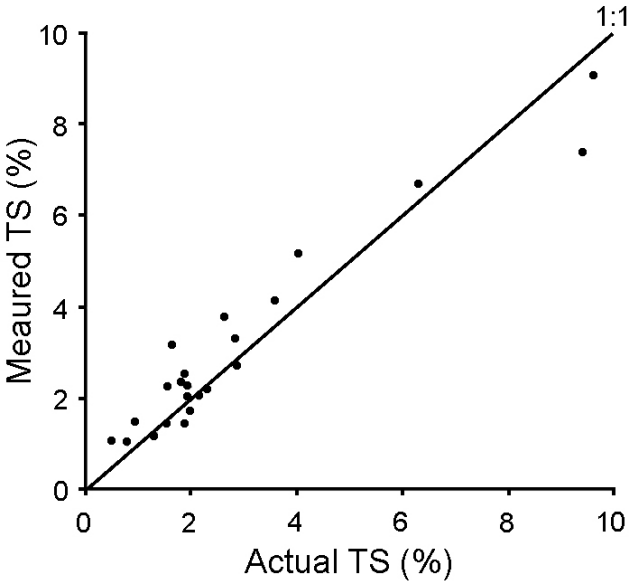

Fig. 5. Validation results for TS.

Malley et al. (2002) measured moisture content (inverse of TS) (r^2 = 0.94, RPD = 4.11, and RER = 16.35) of hog manure with a degree of success comparable to that achieved in this study. The same authors also measured various forms of P (r^2 = 0.79 – 0.99, RPD = 2.18 – 8.46, and RER = 8.45 – 26.72) and K (r^2 = 0.87, RPD = 2.78, and RER = 9.11) with more success than what was achieved here. Treatment of spectral data with first and second order derivatives (as done by Malley et al. 2002) could be considered to improve the performance of calibration equations for P and K.

In two studies of hog manure by Millimier et al. (2000), TKN (r^2 = 0.829 - 0.897 and RER = 8.2 - 9.8), TS (r^2 = 0.920 - 0.947 and RER = 11.1), and P (r^2 = 0.688 – 0.783 and RER = 6.8 - 8.4) were measured with success similar to that which was achieved in this research. Models predicting K (r^2 = 0.840 -

0.887 and RER = 8.9 - 9.0) were more accurate than those generated in this research. In studies of beef feedlot manure by the same author, measurements of TS (r^2 = 0.955 and RER = 13.6), TKN (r^2 = 0.817 and RER = 12.4), and P (r^2 = 0.764 and RER = 7.6) were comparable to results obtained in this research. However, measurement of K (r^2 = 0.905 and RER = 12.0) was more successful than what was reported here.

Reeves (2001) measured various constituents in poultry manure, including various forms of N (r^2 = 0.710 – 0.980), moisture (r^2 = 0.838 – 0.847), P (r^2 = 0.341 – 0.616), and K (r^2 = 0.430 – 0.625). These results are similar to the results obtained in this research, where measurement of TKN and TS were more successful than measurements of P and K. Ye et al. (2001) also measured nutrients in poultry manure. Predictions of TS (r^2 = 0.99 and RER = 24.9), TKN (r^2 = 0.91 and RER = 12.64), P (r^2 = 0.81 and RER = 8.92), and K (r^2 = 0.76 and RER = 6.69) had results comparable to this work. Also, these results were similar to the results obtained in this research, where measurement of TKN and TS were more successful than measurements of P and K.

SUMMARY

Multiple linear regression was used to develop calibration models for predicting TS, TKN, P, and K in Saskatchewan hog manure. Calibration models for TS and TKN achieved good results, while those for predicting P and K were less successful. Additional treatments of the spectral data (first and second order derivatives) and alternative methods for deriving calibration equations (PLS) could be considered to improve the performance of the predictive models.

REFERENCES

Dagnew, M.D. 2002. Reflectance spectroscopy sensing of hog manure nutrients. M.Sc. thesis. Department of Agricultural and Bioresource Engineering, University of Saskatchewan. Saskatoon, SK.

ETL. 2000. Price list. Enviro-Test Laboratories, Saskatoon, SK.

Hruschka, W.R. 1987. Data analysis: Wavelength selection methods. In *Near-Infrared Technology in the Agricultural and Food Industries*, eds. P.C. Williams and K.H. Norris, 35-55. St. Paul, MN: American Association of Cereal Chemists.

Malley, D.F., L. Yesmin and R.G. Eilers. 2002. Rapid analysis of hog manure and manure-amended soils using near infrared spectroscopy. *Soil Science Society of America Journal* 66: 1677-1686.

Millmier, A., J. Lorimor, C. Hurburgh, C. Fulhage, J. Hattey and H. Zhang. 2000. Near-Infrared sensing of manure nutrients. *Transactions of the ASAE* 43(4): 903-908.

Prairie Swine Centre. 2000. Pork Production Reference Guide. Saskatoon, SK: Prairie Swine Centre Inc.

Reeves, J.B. 2001. Near-infrared diffuse reflectance spectroscopy for the analysis of poultry manures. *Journal of Agricultural Food Chemistry* 49: 2193-2197.

SAS. 1999. SAS/STAT user's guide in: SAS online Doc®, version 8. Cary, NC: SAS Institute Inc.

Velasco, L. and W.J. Gruneberg. 1999. Analysis of dry matter and protein contents in fresh yam bean tubers by near infrared reflectance spectroscopy. *Communications in Soil Science and Plant Analysis* 30(13&14):1797-1805.

Williams, P.C. 1987. Variables affecting near-infrared reflectance spectroscopic analysis. In *Near-infrared Technology in the Agricultural and Food Industries*, eds. P. Williams and K. Norris, 143-166. St. Paul, MN: American Association of Cereal Chemists.

Ye, W.Y., J.C. Lorimor and C.R. Hurgburgh. 2001. Application of near-infrared spectroscopic technique for determination of nutrient contents in poultry manures. In *Proceedings of International Symposium Addressing Animal Production and Environmental Issues*, 119-126. Raleigh, NC: Agriculture and Life Sciences, North Carolina State University.