The Determination of Total N, Total P, Cu and Zn in Chicken Manure Using Near Infrared Reflectance Spectroscopy

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Abstract

In this study, the 74 chicken manure samples from a chicken farm were used to take the diffuse reflection spectra from 12500 to 4000 cm^{-1} by FT-NIR spectrometer. The total N, total P, Cu and Zn of chicken manure samples were predicted by NIR spectra. For the samples of each component, an ascending order was arranged and they were divided into calibration set and prediction set according to their content. Partial least square regression (PLSR) method was applied to construct the calibration model. Results showed that the correlation coefficients of the calibration model for total N was 0.69, the root mean square error of calibration (RMSEC) was 0.66, the root mean square error of prediction (RMSEP) was 0.80. For the models of total P, Cu and Zn, the results were r=0.86, RMSEC=0.29, RMSEP=0.34; r=0.95, RMSEC=3.46, RMSEP=5.71; r=0.94, RMSEC=14.13, RMSEP=25.21, respectively. The results indicated that the NIR spectroscopy was useful to non-destructively determine the content of total N, total P, Cu and Zn of chicken manure. As a complementary detecting method to the conventional analysis, NIR spectroscopy could significantly improve the detecting efficiency.

Key words: near infrared spectroscopy, chicken manure, total N, total P, Cu, Zn

1. Introduction

In the last decades, intensive livestock operations produced considerable amounts of animal manure that may cause serious environmental problems [1]. China is one of the largest producers of animal manure in the world, with an annual output of more than 3 billion tonnes[2]. Composting is an appealing solution for sustainable management of animal manure especially the chicken manure[3]. Use of composting results in a stabilized, mature, deodorized and hygienic product, free of pathogens and rich in humic substances, which is environmentally friendly and marketable as an organic amendment or fertilizer[4,5].

The parameters established by the legislation for marketable composts are electrical conductivity (EC), total organic matter (TOM), total organic carbon (TOC), total nitrogen(TN) and C/N ratio, macronutrient contents (N, P, K) and potentially pollutant element concentrations (Fe, Cu, Mn and Zn)[6]. The determination of these important parameters of composts required numerous reagents, skilled labors and expensive analytical equipments. Consequently, a more convenient and reliable method is necessary.

Near-infrared spectroscopy (NIR) (800-2500 nm), which reflects the overtones and combinations of fundamental vibrations of C–H, O–H and N–H bonds, has been widely used for quantitative and qualitative analysis for organic components in petrochemical, agricultural and pharmaceutical field**[**7**]**. Previous study have also indicated that one of the mechanism for measuring heavy metals by NIR was their inter correlation with organic compounds**[**8**]**. In recent years, NIR was also applied as an inexpensive tool for rapid analysis of important component in animal manures **[**9,10,11,12**]**.

The purpose of this study was to explore the feasibility of analyzing organic and inorganic components of chicken manure using NIR simultaneously.

2. Materials and methods

2.1 Sample Preparation and chemical analysis

In this study, the chicken manure samples were collected from a chicken farm from Heishan county, Liaoning Province. The samples were dried at 65 ^{o}C in a forced-air drier to a constant weight and ground to pass a 1 mm screen for latter analysis. In total, 74 samples were prepared.

2.2 NIR Spectra Collection

NIR spectra were recorded by a Fourier transformed near-infrared spectrometer (IFS 28/N, BRUKER, Germany) with integral sphere accessory. The ground chicken manure was filled into a cylindrical quartz cup with 20 mm depth to insure that light did not permeate the sample. The cylindrical cup was rotated slowly to assure fine sample distribution. And the reflectance spectra were recorded within the band between 12500 and 4000 cm^{-1}(800-2500 nm), at 16 cm^{-1} interval. For each sample, the spectra were scanned 64 times and the average spectrum was obtained.

2.3 Measurement of Total Nitrogen, Total Phosphorus, Cu and Zn

The chemical analyses were performed by the Analysis and Test Center, Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Science. The total nitrogen (TN) was determined by dry combustion at 975 °C using a PE-2400 C-N Elemental Analyzer (PerkinElmer Corp., USA). The total Phosphorus (TP) was determined according to the method described in NY525-2002, which is the standard of Ministry of Agriculture. The content of Cu and Zn were measured using an acid digestion method with inductively coupled plasma–atomic emission spectroscopy (ICP–AES, PerkinElmer 3300DV) **[**13**]**.

2.4 Data Analysis

The spectra were not being pre-processed since the quality of original spectra was relatively high. Principle component analysis (PCA) was used to explorer the spectra distribution in the latent space. The calibration model between reference values and spectra were constructed by partial least square regression (PLSR). The outliers for each model were eliminated according to the plot of COOK value vs. leverage value **[**14**]**. For each model, the reference value was sorted in an ascending order. Every third sample was selected as calibration set, while the remaining part the prediction set. The calibration set was used for the model construction, while the prediction set was used for the model validation. The optimal number of PLS factors was selected by leave-one-out (LOO) cross validation. The corresponding PCs were selected when the prediction residual error sum of square (PRESS) was the lowest. The predictive performance of the calibration model was evaluated by the correlation coefficient (r) for the calibration set, the standard deviation of calibration (SEC), the standard error of cross-validation (SECV), the standard deviation of prediction (SEP). A good model are supposed to have small SEC, small SEP and high r. The PCA calculation was carried out with the software Unscrambler 9.1 (Camo Corp., Norway), and the PLSR was conducted by MATLAB 7.0 (The Math Works, Inc., Natick, MA, USA).

3. Results and discussion

3.1 The Characteristics of the components of chicken manure

Table 1 shows the composition statistics in calibration sets and validation sets for total N, total P, Cu and Zn, respectively, which include the number of samples, the mean, standard deviation and range value. It could be seen that the components of prediction set full in the scope of calibration set, which assured the representative of the calibration models.

3.2 NIR Spectra and the PCA plots of chicken manure

The full wavelength range of the spectra was 800-2500 nm. The original spectra were shown in **Figure 1**. The spectra had several absorbance peaks at the wavelength of about 1135 nm, 1340 nm, 1540 nm, 1657 nm, 1870 nm, 2010 nm, 2235 nm, 2416 nm, indicting rich information was contained in the spectra. The possible water absorption peaks was not obvious because the samples were already dried at 65 °C to a constant weight.

Figure 2 showed the result of PCA analysis. It can be seen that the samples constituted a sample set that has some extent of representative. In addition, the first and second principle scores involved 99% variation of the original spectra.

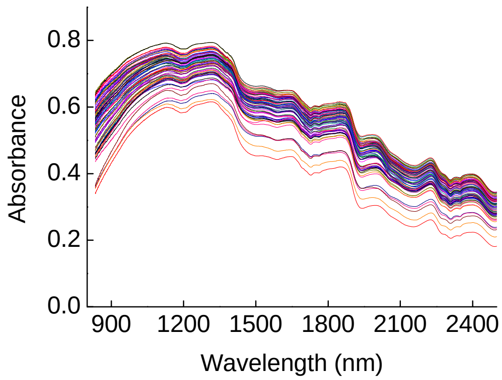

Fig 1. The NIR spectra of chicken manure

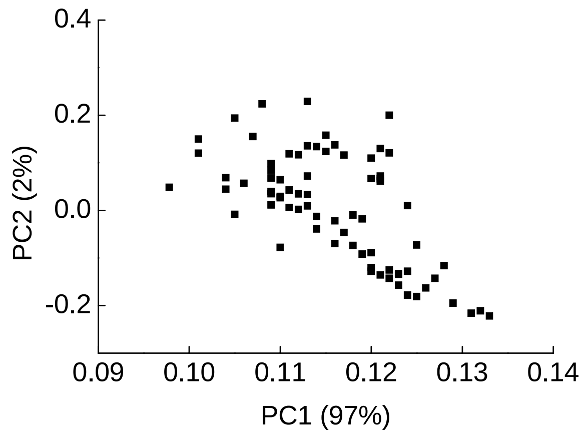

Fig. 2. The PCA score plot of chicken manure

Table 1 The statistic characteristics of calibration set and prediction set for chicken manure

		Number of samples	Min value	Max value	Mean value	Standard deviation
N(%)	Calibration	50	3.51	7.55	5.36	0.91
	Prediction	24	3.55	6.79	5.29	0.85
P(%)	Calibration	42	1.73	4.12	2.86	0.56
	Prediction	21	1.85	3.88	2.86	0.55
Cu(mg/Kg)	Calibration	47	23.41	64.22	41.93	10.85
	Prediction	23	23.80	57.24	41.44	10.53
Zn(mg/Kg)	Calibration	44	144.63	291.98	222.83	39.91
	Prediction	22	145.16	291.42	222.44	40.97

3.3 The Calibration Models for chicken manure

The calibration models of total N, total P, Cu and Zn were shown in Table 2. It can be seen that the total P, Cu and Zn model had high calibration accuracy, with the correlation coefficient (r) of 0.8577, 0.9479 and 0.9352, respectively. Figure 3 shows that the NIR predicted value of total P, Cu and Zn and its reference value were closely arranged with the 45° line, indicating the prediction error was low. The above result suggested that total P, Cu and Zn of chicken manure could be measured by NIRS. The measurement of Cu and Zn were the indirect relation between metal elements and NIR spectra. Previous study have indicated that one of the mechanism for measuring heavy metals by NIR was their inter correlation with organic compounds**[8]**. For the Zn model of compost of pig manure on fresh and dried basis, the R^2 and r^2 values were about 0.69 and 0.6 (Huang et al., 2008). The current Zn model had higher calibration accuracy than that of previous study **[15]**.

The calibration model of total N, however, showed relatively lower accuracy. In the calibration set, NIR spectra and total N had some certain relationship, with the correlation coefficient (r) of 0.6923, which was much lower than that of total P, Cu and Zn model.

According the scatter plot, the NIR predicted total N and its reference value were also distributed aside the 45° line (see Figure 3). However, they were not as close as that of Cu and Zn, indicating that the prediction error was relatively high. The calibration results suggested that although NIR spectra had some extent of relation with total N, the prediction accuracy could not satisfy the requirement of quantitative measurement. Future research may focus on how to improve the accuracy of total N model.

Table 2. The statistic results of calibration models for chicken manure

	PLS factors	r	SECV	SEC	SEP
N	4	0.6923	0.7532	0.6552	0.8047
P	6	0.8577	0.3822	0.2888	0.3418
Cu	5	0.9479	4.3503	3.4595	5.7103
Zn	8	0.9352	23.4447	14.1337	25.2114

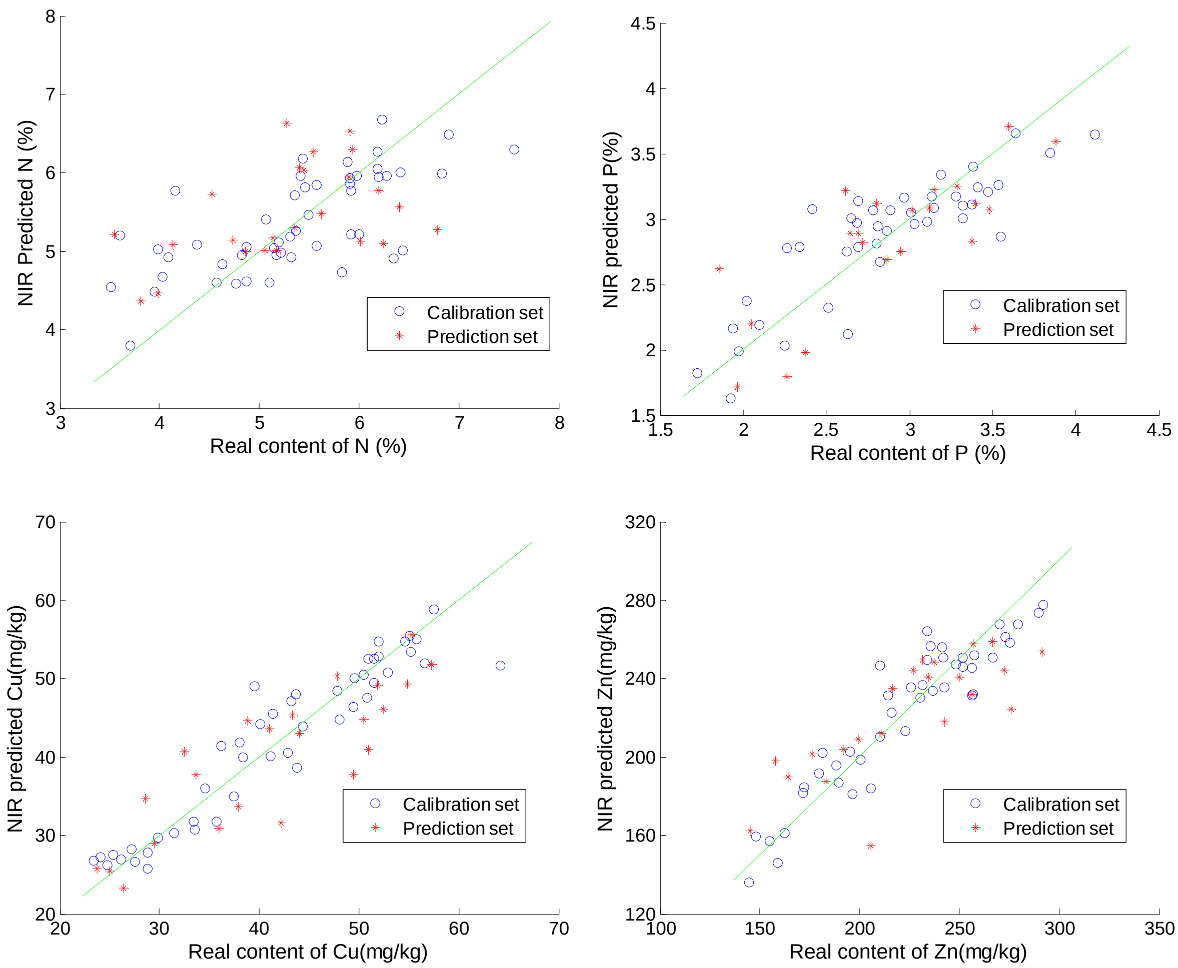

Fig 3. The scatter plots of reference values and NIR predicted values for the components of chicken manure

4. Conclusions

The current study explored the simultaneous evaluation of organic and inorganic components of chicken manure using NIRS. The results showed that the NIRS technique could be a complementary detecting method to the conventional analysis. However, further research is needed to improve the prediction precision of calibration models by enlarging the number and range of samples. The present study only constructed the linear calibration models for the four components of chicken manure. In order to improve the precision of models, future studies may apply non-linear methods such as artificial neural networks to build the non-linear relation between spectra and components.

Acknowledgements

This work was supported by Major projects on control and rectification of water body pollution（2008ZX07425-001）

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