

## Prediction of Heavy Metal Content in Compost Using Near-infrared Reflectance Spectroscopy

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**ABSTRACT :** Since the application of relatively high levels of heavy metals in the compost poses a potential hazard to plants and animals, the content of heavy metals in the compost with animal manure is important to know if it is as a fertilizer. Measurement of heavy metals content in the compost by chemical methods usually requires numerous reagents, skilled labor and expensive analytical equipment. The objective of this study, therefore, was to explore the application of near-infrared reflectance spectroscopy (NIRS), a non-destructive, cost-effective and rapid method, for the prediction of heavy metals contents in compost. One hundred and seventy two diverse compost samples were collected from forty-seven compost facilities located along the Han river in Korea, and were analyzed for Cr, As, Cd, Cu, Zn and Pb levels using inductively coupled plasma spectrometry. The samples were scanned using a Foss NIRSystem Model 6500 scanning monochromator from 400 to 2,500 nm at 2 nm intervals. The modified partial least squares (MPLS), the partial least squares (PLS) and the principal component regression (PCR) analysis were applied to develop the most reliable calibration model, between the NIR spectral data and the sample sets for calibration. The best fit calibration model for measurement of heavy metals content in compost, MPLS, was used to validate calibration equations with a similar sample set (n=30). Coefficient of simple correlation (r) and standard error of prediction (SEP) were Cr (0.82, 3.13 ppm), As (0.71, 3.74 ppm), Cd (0.76, 0.26 ppm), Cu (0.88, 26.47 ppm), Zn (0.84, 52.84 ppm) and Pb (0.60, 2.85 ppm), respectively. This study showed that NIRS is a feasible analytical method for prediction of heavy metals contents in compost. (*Asian-Aust. J. Anim. Sci.* 2004, Vol 17, No. 12 : 1736-1740)

**Key Words :** Compost Quality, NIRS, Calibration Equation, Coefficient of Multiple Determination, Standard Error of Prediction

### INTRODUCTION

Intensive animal operations produce considerable amounts of livestock manure that may give serious environmental problems (CAST, 1996; Gay et al., 2003). On the other hand, livestock manure can be reused as organic fertilizer for agricultural purposes (Shi et al., 1999). Composting that has been defined as a controlled-microbial aerobic decomposition with the formation of stabilized organic materials, is one of more efficient methods of animal waste disposal because it enables recycling of organic matter (Goluke, 1973; Garcia et al., 1992; He et al., 1995; Greenway and Song, 2002).

Although animal manure compost is likely to improve biological, chemical and physical properties of the soil, the application of compost to the soil matrix is of great concern because it may lead to the accumulation of heavy metals in the soil (Veeken and Hamelers, 2002). Several heavy metals, including Zn, Cu, As, Co, Fe, Mn and Se, are added to animal diets for various purposes, resulting in a high concentration of heavy metals in animal waste (Payne et al., 1988; Sims and Wolf, 1994). Continuous application of Cu,

Zn and Mn-rich manure compost in agricultural soils may cause the metals to accumulate to toxic levels (King et al., 1990). Once heavy metals are introduced onto cropping land, they may not only be taken up by plants but may also induce water and soil contamination (L'Herroux et al., 1997). Thus, it is important to obtain basic information about the concentrations of heavy metals in compost before they are applied to the soil for crop production.

Currently, heavy metal concentration of compost is analyzed by conventional wet chemical methods. Although these methods are accurate, they need a large quantity of reagents, skilled labor and time for analysis including pre-treatment. Therefore, it is necessary to develop a new analysis method to overcome such drawbacks of conventional chemical methods. As an alternative, the near-infrared reflectance spectroscopy (NIRS), a rapid, non-destructive, cost-effective technique, has been extensively used for qualitative and quantitative analysis in the fields of agriculture (Ru and Glatz, 2000), food, textiles and pharmaceuticals (Osborne et al., 1993). In fact, several researchers have discussed the theory and the practice of NIRS (Buns and Cziuczak, 1992; George and Steele, 1995; Blanco and Villarroya, 2002). In relation to the analysis of inorganic components by NIRS, Hunt and Salisbury (1970) reported that pure metals did not absorb in the NIR region but might be detectable because they were complexed with organic matter.

Ben-Dor and Banin (1995) established several prediction equations using NIRS for prediction of several

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**Table 1.** Total concentration of the heavy metals in the compost by chemical analysis

Heavy metal (mg/kg dm)	Swine manure <sup>1</sup>			Poultry manure <sup>2</sup>		
	Range	Mean	SD*	Range	Mean	SD
Cr	3.40-63.55	15.26	10.27	3.83-35.17	18.93	7.51
As	3.67-39.38	16.47	7.12	4.08-38.18	16.79	9.34
Cd	0.78-3.46	1.51	0.5	0.95-3.68	2.17	0.71
Cu	60.99-399.08	166.23	68.77	28.15-240.40	72.2	37.34
Zn	205.08-794.86	425.77	177.05	106.16-345.04	229.21	55.09
Pb	1.69-21.55	8.12	4.2	5.29-23.54	10.62	3.61

<sup>1</sup> The number of samples was 114. <sup>2</sup> The number of samples was 58. \* Standard deviation.

soil properties. Malley and Williams (1997) demonstrated that the prediction of heavy metal concentrations in freshwater sediment by NIRS is feasible. However, no study has been conducted to analyze the heavy metal concentration of animal waste compost utilizing the NIRS method. Therefore, the objective of this study was to examine the possibility of predicting heavy metals concentration in compost with animal manure by using NIRS.

## MATERIALS AND METHODS

### Compost sampling and preparation

The types of composting systems were nearly enclosed discharge shutes and agitated bin systems. Most facilities were designed for animal manure conditioned with sawdust and/or wood chips. One hundred and seventy two compost samples (1 kg each) were collected by coring (1 m depth). Each compost core (20-30 cm long) was placed into a polyethylene bag. These include different composting processes (mixing, curing, screening and packing) from the 47 compost facilities located along the Han river, Korea. The samples were dried at 75°C in a forced-air oven for 48 h then ground through a 1 mm sieve for metal analysis and NIRS scanning. After grounding and scanning samples, they were randomly divided into two groups to make a calibration sample set (n=142) and a validation sample set (n=30) by measuring Mahalanobis distance (H) (Shenk and Westerhaus, 1991).

### Chemical analysis

The dried and ground samples were digested by HNO<sub>3</sub> and HClO<sub>4</sub> (5:1 ratio v/v) to determine heavy metal concentrations in the compost (Petruzzelli et al., 1986). A 1.000±0.01 g subsample was digested after adding 36 ml of acid mixture solution. Zn, Cu, Cr, As, Cd and Pb was determined in the resulting solution by inductively coupled plasma (ICP) emission spectrometry (Shimadzu, ICPS-1000 IV, Japan). All concentration data reported in this paper is for duplicate samples on dry matter basis.

### NIRS analysis

All the samples were scanned using the NIRSystem

Model 6500 scanning monochromator (Foss-NIRSystems, Silver Spring, MD, USA). Prior to obtaining the NIR spectra of sample, a ceramic standard was used for the reference spectra. All spectra were collected with the reflectance mode from 400 to 2,500 nm at 2 nm intervals. The spectral reflectance curves were recorded as log 1/R (R=diffuse reflectance) before storing in the computer.

### Statistical analysis

The chemical data determined by conventional wet chemical methods were added to the corresponding NIRS spectral files using the WinISI II. (Ver. 1.04) which is software developed by the Infracsoft International, LLC (FOSS NIRSystem/TECATOR, 1999). All spectral data were subjected to the same mathematical treatments for noise reduction, baseline correction and isolation of spectral information relating to sample chemistry. The modified partial least squares (MPLS), the partial least squares (PLS) and the principal component regression (PCR) analysis were applied to develop a best fit calibration equation on the basis of a low standard error of calibration (SEC) and a large coefficient of multiple determination (R<sup>2</sup>). It is necessary to validate with unknown samples the selected calibration equation during routine NIRS analysis. Coefficient of simple correlation (r) between chemical measurement and NIR prediction was calculated from the above calibration equations. Standard error of calibration (SEC) and prediction (SEP) are calculated for examining the equation performance and defined by the following equation (1)-(2) (Davies and Grant, 1987; Marten et al., 1989).

$$SEC = \{ \sum (X_i - Y_i)^2 / (N - p - 1) \}^{0.5} \quad (1)$$

$$SEP = \{ \sum (X_i - Y_i)^2 / (N - 1) \}^{0.5} \quad (2)$$

Where,

X<sub>i</sub>: Value determined by conventional analytical method.

Y<sub>i</sub>: Value determined by NIRS.

N: Number of samples.

p: Number of terms in the calibration equation.

**Table 2.** Comparison of the regression models for the heavy metal measurements in the compost

		Cr	As	Cd	Cu	Zn	Pb
MPLS <sup>1</sup>	R <sup>2</sup> *	0.88	0.76	0.82	0.82	0.85	0.64
	SEC**	3.66	3.69	0.24	25.07	45.99	2.48
PLS <sup>2</sup>	R <sup>2</sup>	0.88	0.75	0.81	0.82	0.82	0.62
	SEC	5.77	3.75	0.25	25.43	50.92	2.45
PCR <sup>3</sup>	R <sup>2</sup>	0.67	0.72	0.81	0.61	0.54	0.59
	SEC	4.99	3.97	0.26	46.38	86.93	2.55

<sup>1</sup> Modified partial least squares. <sup>2</sup> Partial least squares. <sup>3</sup> Principal component regression.

\* Coefficient of multiple determination. \*\* Standard error of calibration.

## RESULTS AND DISCUSSION

The concentrations of the selected heavy metals (Cr, As, Cd, Cu, Zn and Pb) in the compost with swine and poultry manure are presented in Table 1. The mean concentration of Zn is the highest, followed by Cu, As, Cr, Pb and Cd in compost with swine manure. It varied widely with animal species, age, feedstuff, physical conditions and nutrient utilization. The concentrations of the heavy metals in the compost, in general, were much higher than those in most agricultural soils, particularly Cu and Zn. The concentrations of total metals in the compost-amended soils were not critically high, however repeated applications of compost to soil can accumulate and eventually high levels of heavy metals can cause the contamination of food chains and harm people (Petruzzelli, 1989). For instance, Cd is readily taken up and accumulated by plants in appreciable quantities, although it is not essential for plant growth (Kabata-Pendias and Pendias, 1992).

Table 1 showed that Zn and Cu were the highest metal concentrations in the swine and poultry manure compost with average concentrations of 425.8 mg Zn/kg, 166.2 mg Cu/kg and 229.2 mg Zn/kg, 72.2 mg Cu/kg DM, respectively (Table 1). The concentrations of As, Cr and Pb were <20 mg/kg DM in all composts analyzed. The concentration ranges for each metals were wide among compost facilities and composting processes. Fleming and Mordenti (1991) reported that the mean Zn concentration in Belgian cattle manure was 580 mg/kg DM. However it was found that cattle manure was <200 mg Zn/kg DM in this study and a survey of Swiss manures (Menzi and Kessler, 1998). Also, Nicholson et al. (1999) reported that the mean concentrations in pig manure were 500 mg Zn/kg and 360 mg Cu/kg DM, and concentration of other metals such as Cd, Cr and Pb were usually below 5 mg/kg DM. Generally, the composition and concentration of heavy metals of animal manures were largely a reflection of those of the feeds consumed. This result, therefore, suggested that the raw material i.e. animal waste was the major factor contributing to heavy metal concentrations in compost.

It is important to choose selection of samples, sample analysis, spectrum collection, and calibration development on account of the empirical nature of NIR spectroscopy.

The pre-treatment of spectral data that operates on purified spectra, either fully or partly eliminates the systematic error that can be caused by the various factors. The data pre-treatment in this study was applied to the raw spectra to reduce the light scatter and the baseline offsets from variations.

The second derivative of each NIR spectrum was more precise on calibration model than the raw data or first derivative (results not presented) because it displayed the baseline bands more clearly. Chen et al. (2002) reported that the second derivative spectra were better suited for calibrating and predicting for analyzing oil content of instant noodles. According to Reeves and McCarty (2001), however, optimal calibrations were achieved using the first derivative spectra when determining various constituents of agricultural soils.

As presented in Table 2, the modified partial least squares (MPLS), the partial least squares (PLS), and the principal component regression (PCR) methods were applied to develop a best calibration model between the NIR spectral data and the chemical analysis data. In most cases, the MPLS was slightly better than the PLS and the PCR. Generally, the most important statistical parameters of the developed calibration equations were the standard error of calibration (SEC) and the coefficient of multiple determination ( $R^2$ ). Lower SEC and higher  $R^2$  values of the calibration equation are considered better and more accurate (Windham et al., 1987; Marten et al., 1989). The best prediction calibration model (MPLS) for Cr, Cd, Cu and Zn gave  $R^2 > 0.80$  between the chemical value and the NIR predicted heavy metal concentration. However the results of calibrations for As and Pb showed that  $R^2$  values were 0.76 and 0.64, respectively. Except for Cd, this calibration is less accurate than that reported by Malley and Willams (1997). This may be because concentration of heavy metal in the samples and heterogeneous sample population in the present study is more variable than that of the study by Malley and Willams (1997).

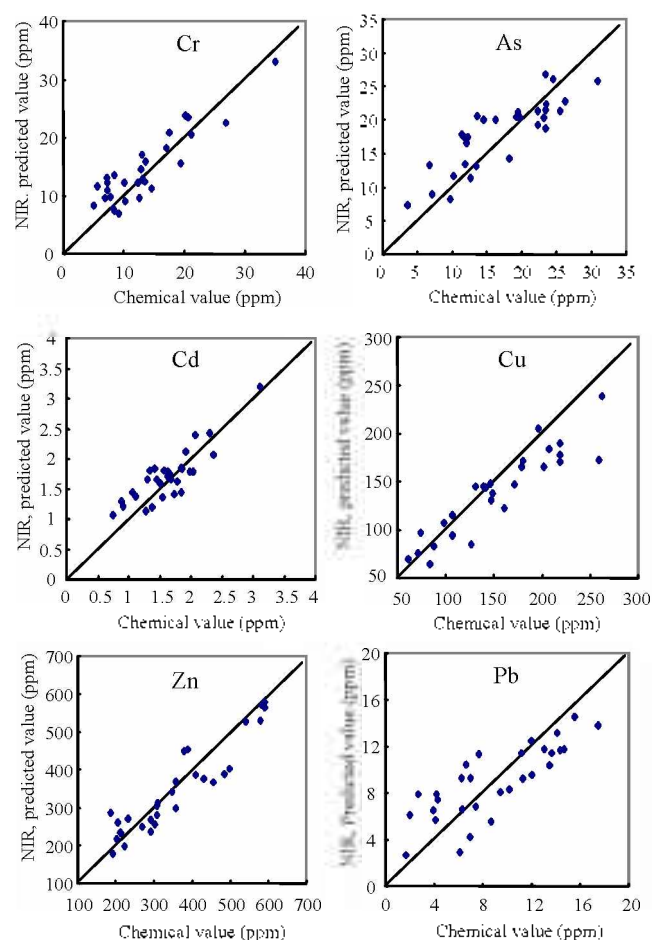
Because the NIRS method is an empirical analysis method, it is necessary that the selected equation should subsequently be validated with an independent sample set. The validation results for selected heavy metals were summarized in Table 3 and graphed in Figure 1. The

**Table 3.** Results of the best calibration (MPLS model) and validation for determining heavy metals in the compost

Heavy metal	Calibration		Validation	
	R <sup>2</sup> *	SEC**	r***	SEP****
Cr	0.88	3.66	0.82	3.13
As	0.76	3.69	0.71	3.74
Cd	0.82	0.24	0.76	0.26
Cu	0.82	25.07	0.88	26.47
Zn	0.85	45.99	0.84	52.84
Pb	0.64	2.48	0.60	2.85

\* Coefficient of multiple determination. \*\* Standard error of calibration.

\*\*\* Coefficient of simple correlation. \*\*\*\* Standard error of prediction.

**Figure 1.** Relation of the NIR-Predicted and the reference chemical value for determining the content of heavy metals in the compost. The lines are 1:1 relationships.

selected equation accuracy is expressed as standard error of prediction (SEP). If the calibration was produced correctly, SEP will be close to the SEC and  $r$  will approach to 1.0 (Geladi et al., 1985; Davies and Grant, 1987; George and Steele, 1995). George and Steele (1995) stated that the analyst could feel comfortable with  $r$  values  $>0.9$ , if this value was low ( $<0.5$ ) it is questionable whether NIR is a useful technique for prediction of the constituents being analysed. In this experiment, the  $r$  and SEP values were Cr

(0.82, 3.13 ppm), As (0.71, 3.74 ppm), Cd (0.76, 0.26 ppm), Cu (0.88, 26.47 ppm), Zn (0.84, 52.84 ppm) and Pb (0.60, 2.85 ppm), respectively. It is concluded from this study that it is feasible to predict Cr, Cu and Zn, and it may be feasible to predict As, Cd and Pb by using the NIRS.

## CONCLUSION

There is no work on the prediction of heavy metals content in compost using the NIRS. Three mathematical treatments were used to develop optimal calibration models. The study showed the second derivative performed better than using the log 1/R and first derivative treatment. The MPLS calibration model could predict correlation between the predicted values by the NIRS and the values by chemical analysis better than the PLS or the PCR method. This study showed that the NIRS technique can be a useful method to determine heavy metals content of compost with animal manure. However, further studies are needed to predict specific heavy metals in compost more precisely by accumulating more data and more sample species.

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