Determination of Cr, Zn, As and Pb in soil by X-ray fluorescence spectrometry based on a partial least square regression model

Anxiang Lu[1,2], Xiangyang Qin[2], Jihua Wang[1,2,*], Jiang Sun[3], Dazhou Zhu[2], and Ligang Pan[1]

[1] Beijing Research Center for Agri-food Testing and Farmland Monitoring, Beijing, China
[2] Nation Engineering Research Center for Information Technology in Agriculture, Beijing, China
[3] Beijing Municipal Station of Agro-Environmental Monitoring, Beijing, China
{Anxiang Lu, Xiangyang Qin, Jihua Wang, Jiang Sun, Dazhou Zhu,
Ligang Pan, wangjh}@nercita.org.cn

Abstract. Soil samples were collected from five provinces over China, including Beijing, Xinjiang, Heilongjiang, Yunnan, and Jiangsu. Heavy metal Cr, Zn, Pb and As in soils were analyzed by a portable X-ray fluorescence spectrometry (XRF). For predicating metal concentration in soils, a partial least square regression model (PLSR) was established. After cross-calibration, the correlation coefficients for validation (R) of value predicted by PLSR model against that measured by AAS and AFS for Cr, Zn, Pb and As was 0.984, 0.929, 0.979, and 0.958, square error of validation (SEP)was 108 mg kg^{-1}, 117 mg kg^{-1}, 116 mg kg^{-1}, and 167 mg kg^{-1} for metals concentration from about 100 to 1500 mg kg^{-1}, and the relative square error of validation(RSEP) was about 14.5 %, 15.6 %, 14.9 %, and 21.0 %. These results indicated XRF based on PLSR model could be applied for determination of Cr, Zn, Pb and As in soil, and would be an effective tool for rapid, quantitative monitoring of metal contamination.

Keywords: Heavy metal, Soil, Partial least square regression, X-ray fluorescence spectrometry

1. Introduction

Contamination by metals in the soil has become widespread in a global context. Wastewater irrigation, solid waste disposal, sludge applications, vehicular exhaust and industrial activities are the major sources of soil contamination with heavy metals. Increasing metal pollution has severely disturbed the natural ecosystem and harmed human health through food chain.[1, 2] Numerous programs have been

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conducted to monitor heavy metal in soils by governments or institutions all over the world. [3, 4]

Heavy metals in soil can be measured by several conventional analytical techniques including electro- chemical methods, chromatographic separation and spectroscopic techniques etc. Especially, atomic absorption spectroscopy (AAS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) have been the official reference methods, preceded by time-consuming acid digestions which are also subject to possible contamination to sample and additional pollution to laboratory environment. Compared with traditional methods, X-ray fluorescence spectroscopy (XRF) has some potential advantages for soil heavy metal analysis, it is non-destructive with rapid throughout and simple sample preparation avoiding acid digestion and the sensitivity of $\sim$ 10 mg kg^{-1} is appropriate for field screening for most metals.[5] For example, field XRF can easily provide detection limits for lead-in-soil of less than 100 mg kg^{-1}, well below typical regulatory levels of 300 to 1500 mg kg^{-1}. Actually, XRF has been widely applied in metal determination in variety of environmental samples, such as soil, sediment, dust, rocks. [6, 7, 8]

However, the accuracy of the measurement by XRF can be affected by the sample characteristics, e.g. moisture content, density, flatness of the surface, particle size, soil type.[9] For soil and other complex matrices, empirical methods for calibration can be difficult or cumbersome, and theoretical calibration methods such as fundamental parameters models are not always viewed as reliable.[10] Partial least squares regressions (PLSR) are multivariate statistical techniques that have been applied to different sciences to obtain calibration models as an alternative to linear regressions. This statistical method has provided good predictive models for the simultaneous analysis in complex matrices.[11] In the paper, by combining XRF analysis with the PLSR model, we have developed a relatively uncomplicated technique to determine the Cr, Zn, Pb and As in a collection of soil samples. This approach will almost certainly prove to be applicable to other metals of environmental samples as well. This technique could be useful for the semi-quantitative or quantitative determination of metals in variety of environmental solid samples.

2. MATERIALS AND METHODS

2.1 Sample Preparation

Topsoil (0~20 cm) samples were collected from five provinces in China, including Beijing, Xinjiang, Heilongjiang, Yunnan, and Jiangsu. Soil samples were air-dried and passed through a 2.0 mm sieve, homogenized and stored at 4℃ until use. An incubation experiment was conducted with 500 g of each soil in plastic pot to simulate metal pollution. Heavy metals Cr, Zn, Pb and As were added as nitrate salts (Cr (NO$_3$)$_3$, Zn (NO$_3$)$_2$, Pb (NO3)2 and NaAsO$_2$) in aqueous solution and then mixed with soils thoroughly. The amounts of metals added to soils were 100, 200, 400, 600,

800, 1000 and 1500 mg kg-1 of Cr, Zn, Pb, and As (metal/soil), respectively. These soils were incubated for 2 months, and air-dried for analysis. And extra pots without addition of heavy metals were simultaneously prepared as blank sample.

2.2 XRF Spectra Collection

Cr, Zn, Pb and As in soil samples were simultaneously analyzed by a portable XRF (XRF7), obtained from Beijing Purkinje General Instrument. The instrument parameter and operating condition was listed in table 1. Prior to sample analysis, an internal instrument calibration was performed. All samples were analyzed using the bulk mod for soils. Each sample was analyzed for 300 s through a small plastic cup covered with SDI mylar film.

Table 1. The instrument parameter and operating condition.

	Instrument parameter and operating condition
X-ray tube	Ag
Filter	Al + Mo
Detector	Si-PIN
V	30 kV
I	40 μ A
Cr-K α	5.414 eV
Zn-K α	8.638 keV
As-K Β	11.725 keV
Pb-L Β	12.611 keV

2.3 Measurement of Heavy Metals by Standard Methods

Soil samples were digested using the standard method. 1.0 g soil was placed in a 50 ml round bottom flask with 10 ml aqua regia (HCl :HNO_3 = 1:3). The solution was kept at room temperature overnight before a water condenser was attached and the solution heated to boiling for 2 h. 10 ml of water was added down the condenser before filtration of the mixture through using a Whatman No. 42 filter. The filtered residue was rinsed twice with 5mL of water and the solution was made up to 50mL. All solutions were prepared with 18.3 MΩ deionised water. The above procedure was also used to obtain a blank and control samples and all samples were blank-corrected. Concentration of Cr, Zn, Pb and As in digested sample solution were analyzed using AAS and AFS (Atomic Fluorescence Spectrometry). Reference soil sample ESS-1 was also analyzed as quality control sample.[12,13]

2.4 Data Analysis

XRF spectra was exported from XRF 7 (version 1.0) software in CSV format to MS-Excel (version 2003) for spectral analysis.

The main idea of PLSR is to get as much concentration information as possible into the first few loading vectors. One of the main advantages of PLSR is that the resulting spectral vectors are directly related to the constituents of interest. In this study, PLSR and leave-one-out cross-validation were used for establishing calibration models for Cr, Zn, Pb and As respectively. Leave-one-out cross-validation estimated the prediction error by splitting all samples into two groups. One was reserved for validation, and the other was used for calibration. The process was repeated until all the samples had been used once in the validation set. The optimum number of factors used in PLSR was determined by the lowest value of predicted residual error sum of squares (PRESS). In this study, PLSR were performed using the Matlab (version 7.0) from Math-Works Inc.

The statistics used for estimating the performance of the calibration models developed by PLSR included correlation coefficients for validation (R)and root mean square error of validation (SEP).

$$R = \sqrt{[1 - \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - y_m)^2}]}$$

$$\tag{1}$$

$$SEP = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i)}$$

$$\tag{2}$$

where y_i is the reference value of the i-th sample, $\hat{y}_i$ is the predicted value of the i-th sample, y_m is the average of the referenced value of the validation set, and n is the number of samples in the validation set.
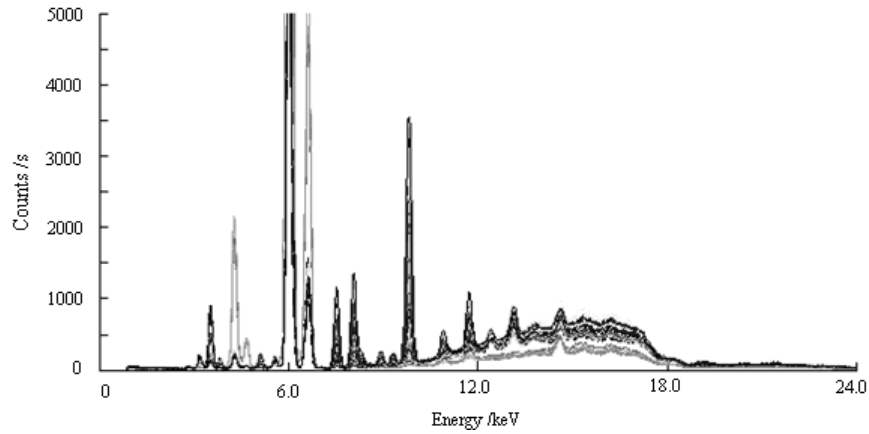
Fig. 1. X-ray fluorescence spectra of the soil samples

3. RESULTS AND DISCUSSION

Figure 1 shows the XRF spectra of soil samples. The mail features of the soil samples are energy bands between 3.0 keV to 18.0 keV. From the characteristic energy of metals listed in table 1, the relevant energy of electron volt at 5.414 keV, 8.638 keV, 11.725 keV and 12.611 keV and close range represents the concentration of Cr, Zn, As and Pb respectively. Therefore spectra in these energy ranges: 5.399 ~ 5.429 keV, 8.623 ~8.653 keV, 11.710 ~11.740 and 12.595 ~12.625 keV were used for developing PLSR models for Cr, Zn, As and Pb separately.

By means of full cross-validation with in PLSR method, the selection of optimal PLS factor (number of latent variables) was important. The number of latent variables for heavy metals is obtained according to the smallest PRESS. The number of latent variables for all the metals was 6 the same.

Table 2. The results of calibration models for metals.

	R	SEP (mg kg^{-1})	RSEP (%)
Cr	0.984	109	14.5
Zn	0.929	117	15.6
As	0.979	116	14.9
Pb	0.958	168	21.0

Using the optimum parameters for PLSR, the calibration models for Cr, Zn, As and Pb were established respectively. Table 2 showed the results of calibration models for metals. It can be seen that metal model had high calibration accuracy, the correlation coefficient (R) was 0.984, 0.929, 0.979, and 0.958 for Cr, Zn, As and Pb. Its prediction ability was also satisfied, the relative square error of validation (RSEP) were 14.5 %, 15.6 %, 14.9 % and 21.0 %, The XRF predicted metal concentration and

its reference value were closely arranged with the 45° line (Figure 2), indicating the prediction error was low. The above result suggested that concentration of heavy metal Cr, Zn, As and Pb in soil could be measured by XRF combined with PLSR model easily.
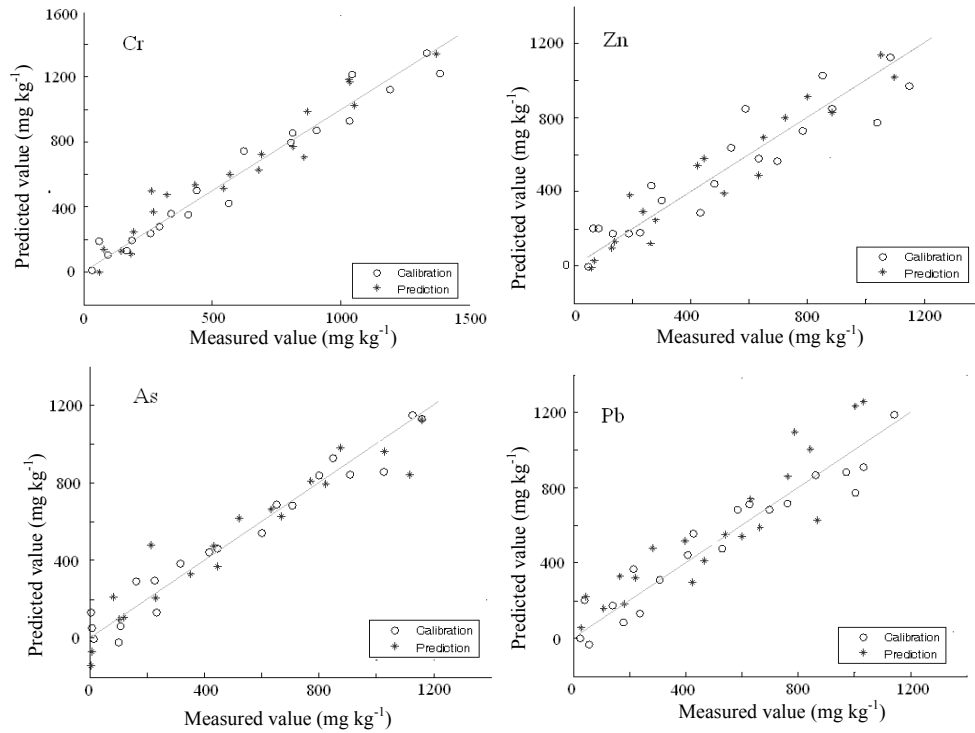

Fig. 2. Scatter plots between measured and predicted value by PLSR model

4. Conclusion

Quantitative or semi-quantitative analyses for Cr, Zn, As and Pb in soil can be performed using XFR with a calibration model established by the method of PLSR. Creating PLSR calibration models for XRF especially useful if suitable well characterized reference standards are not available or the fundamental parameter method is inaccessible or unsatisfactory. As demonstrated, this model is suitable for soil samples of different types without a set of standards for each site. Certainly, XRF with PLSR model approach can be considered as a useful tool for fast screenings, field testing and rapid identification of heavy metals in soil.

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