HEAVY METAL PB^{2+} POLLUTION DETECTION IN SOIL USING TERAHERTZ TIME-DOMAIN SPECTROSCOPY FOR PRECISION AGRICULTURE

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ABSTRACT

Soil is an important natural resource for human beings. With the rapid development of modern industry, heavy metals pollution in soil has made prominent influences on farmland environment. As a result, the crop yield shall be greatly cut down; and the heavy metals do great harms to human body by food chain. Pb^{2+} is kind of typical heavy metals and its pollution is serious at present. The typical existing detection methods are not suitable for agricultural applications. Development of an advanced, safe, efficient and portable detection method for heavy metals content in soil is in an urgent need. This study presents a feasible study of heavy metal Pb^{2+} detection method based on Terahertz Time-domain Spectroscopy (THz-TDS), which is rapid and maybe portable and low cost for future in-field applications. THz is a brand new and safe technology with many unique features. It showed some feasibility for heavy metal detections in soil according to former experiments. A series of experiment were carried out in this study. Soil samples with predefined concentration levels of heavy metal ions Pb^{2+} were carefully prepared. Pressed-slice method was used for the spectra measurement and sample making parameters were determined. The absorption spectra were collected with a THz spectroscopic system in Capital Normal University. Multivariate statistical methods were studied and used to analyze the collected data and establish predication model for Pb^{2+} concentrations. Calibration and prediction models were established based on partial linear regression (PLR) and interval-partial linear regression (i-PLR) methods using the full THz spectrum and the selected THz wavebands respectively. The results showed that the optimized models were able to predict soil heavy metal Pb^{2+} content with a correlation coefficient of 0.81. The method of using THz technology for soil heavy metal Pb^{2+} detection is feasible. However, more investigation on

measurement principles and a large amount of sample tests are still needed. With the detection results, it can be found the heavy metal Pb^{2+} pollution spatial distribution information of the soil in-field and get the "pollution map". Specific measures shall be taken based on the "pollution map" to manage the soil to improve the farmland productivity. This study will provide a reference for heavy metals pollution detection solutions for precision agriculture and sustainable agriculture development.

INTRODUCTION

Precision Agriculture (PA) is a farming management concept based on observing, measuring and responding to inter and intra-field variability in crops. Crop variability typically has both a spatial and temporal component which makes statistical treatments quite involved. Precision agriculture management practices can significantly reduce the amount of nutrient and other crop inputs used while boosting yields (McBratney et al. 2005, and Whelan et al. 2003). With the rapid development of modern industry, heavy metals pollution in soil has made prominent influences on farmland environment. It was reported that, one fifth of China's cultivated lands and more than 217,000 farms in the US have been polluted at different levels by heavy metals. The crop grows in the polluted soil and the heavy metal ions transfer from soil to the plant and agro-products. As a result, the crop yield shall be greatly cut down; and the heavy metals do great harms to human body by food chain. Observing heavy metal pollution status of farmland and making decisions to recover the polluted area according to spatial and temporal variability is also part of Precision Agriculture. Development of an advanced, efficient and feasible detection method for heavy metal content is the first step to observe pollution status of soil. The typical existing detection methods are Atomic Absorption Spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), X-ray and so on; For these existing methods, they are mainly operated in the lab, time-consuming (more than 12 hours), the instruments are very expensive and lack of sensitivity and selectivity (Kou et al., 2009; Li, 2006; Altin et al., 1998; Bambang et al., 2003; Darwish et al., 2001; Ding et al., 2000). They are not suitable for agricultural applications. New methods such as electrochemistry are still immature for practical uses (Malitesta et al., 2005).Development of an advanced, safe, efficient and portable detection method for heavy metals content in soil is in an urgent need.

Terahertz (THz) refers to electromagnetic waves functioning at frequencies of 0.1-10 THz. It lies between micro-wave and infrared bands and is an unexplored region of electro-magnetic region until recent years (Zhang, 2009).

The THz response spectra of substances include transmission spectra and spectral reflectance with plenty of physical and chemical information at THz band. Researchers around the world has paid much attend on it recently. Applications of THz in agriculture have just started. Li, et al. (2010) reported a preliminary study using terahertz time-domain spectroscopy for pecan internal quality detection. The test results showed that nutmeat, shell, and inner separator had different THz absorption characteristics within the waveband of 0.2-2.0THz. Higher water content in insects showed very strong contrast responses to pecan nuts which made the detection of internal insect damages feasible. Li, et al. (2009) applied THz Time Domain Spectroscopy (THz-TDS) to study the spectral characteristics of soil samples amended with CuSO4 and ZnSO4, respectively in the range of 0.2-1.6THz. Three distinct absorption peaks were observed for the two types of sample mixtures. The research implied that the THz-TDS could be used to determine metal concentrations in soils. THz's potentials for many applications especially in some important fields, such as heavy metals pollutions detection in soil based on former research are worth to study through well designed statistical experiments although the THz equipment is still expensive now.

Pb^{2+} is kind of typical heavy metals and its pollution is serious at present. In this research, detection method of heavy metal content in soil using Terahertz Time-domain Spectroscopy (THz-TDS) was detailed studied. Soil samples with Pb^{2+} ion at 30ppm-900ppm were prepared and measured using Terahertz time-domain spectroscopy (THz-TDS) equipment first for preliminary study; then, 30 soil samples with Pb^{2+} were prepared and THz absorption spectroscopy of each sample was measured using THz-TDS equipment; Finally a calibration and prediction model based on Multivariate statistical methods were established and used to analyze the collected data and predict the heavy metal concentrations.

MATERIALS AND METHODS

Sample Preparation

Sample preparation method was first studied at China Agricultural University in 2011. For this research, pure soil was collected from experimental fields (Xiaotangshan Precision Agriculture Demo base, Beijing, China) within the depth of 20 cm. All metal tools were avoided. Pb^{2+} concentration in pure soil was tested in an authorized agency (Puni analyzing & testing center, Beijing, China) to determine their concentrations in the pure soil. The heavy metal ions were from chemical compound $Pb(NO_3)_2$ (Xilong Co.,Ltd, Guangzhou, China). Once concentration of heavy metals in pure soil is lower than the standard value, the following procedures will be carried out. Based on the National Standard for Heavy Metals Pollution (GB15618-1995), a set of soil samples with different heavy metal concentrations were prepared in the lab. 30 concentration levels were selected from 30ppm to 900ppm at the interval of 30ppm for Pb^{2+}.

Calculation: Based on the molecular weight of heavy metal Pb^{2+} in compound $Pb(NO_3)_2$, the required weight of compound for each sample was calculated.

Weighing and labeling: Samples were weighed as the calculated results and labeled based on different concentrations.

Mixing and dissolution: In order to get a unique mixture with Pb^{2+}, we dissolved the mixture in pure water. A glass bar was used to make the solution unique.

Heating: We heated the solution in an oven (Zhonghuan Co., Tianjin, China) at 80℃ for 24 hours. The solid mixture was got.

Grinding: Each solid mixture was grinded into powder for 6 minutes and soil samples were got with particles less than 0.1mm in diameter.

Sealing: All samples were carefully sealed in small labeled bags.

Cleaning: all the instruments were well-cleaned at the end of this preparation.

(a)   (b)

Fig. 1. Samples preparations: (a)Heating. (b)sealing.

THz-TDS system

In this research, Z-2 time domain spectrometer was used to carry out experiments on Pb^{2+} content measurements. It is located at Capital Normal University in Beijing, China. With a ZnTe crystal as a detector, the system offers a broadband spectral coverage of 0.1-3.0 THz and a high-dynamic range measurement in transmission geometries at a 5GHz spectral resolution.
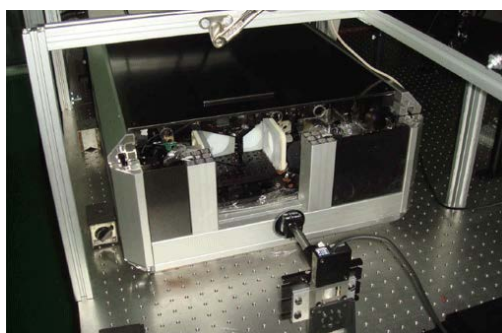
Fig. 2. THz-TDS equipment

Sample-making method

In order to measure the transmission spectroscopy of soil samples in THz band, pressed-slice method was studied and parameters of the preparation process were selected and optimized.
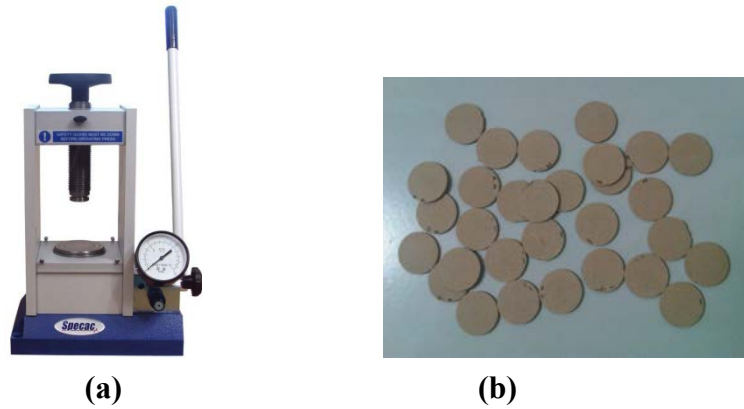

| (a) | (b) |

Fig. 3.THz-TDS equipment: (a) pressed-slice making machine. (b) slices.

Signal attenuation calculation

Absorption coefficient is usually used to reflect the properties of a material (Zhang, 2009; Li, et al., 2010). Based on the Beer-Lambert-Bouguer law, for a solid material, when a parallel beam of monochromatic radiation passes through a homogeneous material, the loss of radiant intensity is proportional to the product of the path length through the material and the initial incident intensity (Equation 1).

$$I = I_0 e^{-(\alpha \times d/2)}$$

(1)

Where I and I0 is the intensity of transmitted signal and the incident light, respectively; α is the absorption coefficient (cm-1); and d (cm) is the thickness of the material. During the experiment, I and I0 can be measured. With the Equation and developed software, the absorption coefficient of testing samples can be calculated.
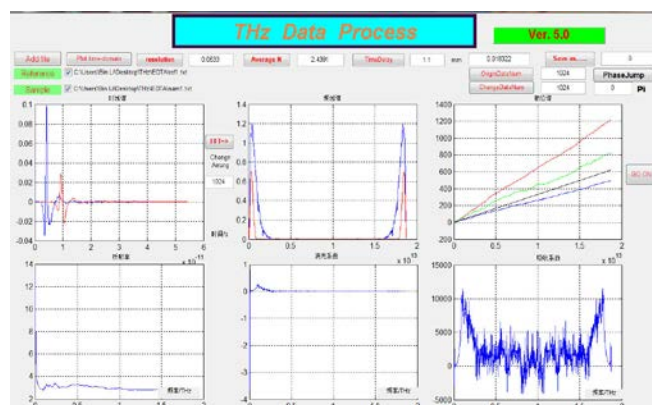
Fig. 4. THz data processing software

Multivariate statistical methods

Partial-least-square (PLS) and Interval Partial-least-square(i-PLS)methods were used to analyze the collected data in this research. PLS (Li, 2006) is a statistical method that bears some relation to principal components regression. It finds a linear regression model by projecting the predicted variables and the observable variables to a new space. The goal of PLS is to predict Y (Chemical values) from X (variables) and to describe their common structure. The Unscrambler software (CAMO Co., Norway) provides PLS algorithms and it was used in this research. When there is too much noise using the full wavelength spectra for modeling, i-PLS algorithm is usually employed. i-PLS was used to select sensitive wavelengths from full THz wavelengths and establish calibration models using these selected wavelengths. It can greatly reduce noise involved in full wavelength spectra. Matlab provides i-PLS toolbox and this algorithm was used for optimizing the model in this research.

RESULTS AND ANALYSIS

Parameters determination of slices

In order to get effective information of samples, parameters for making slices were firstly studied. Pressed-slices under different pressures and thicknesses (Pressure from 0.5-5t, weight from 130-400mg) were made and measured using Z-2 THz equipment at Capital Normal University. The thicker of the slice is, the weaker of the transmission THz spectra is; the heavier of the pressure is, the weaker of the transmission THz spectra is and maybe inner structure of the samples will be destroyed. If it is too thin and pressure is too light, it is difficult to shape the slice. From the actual sample making process and measured curves, parameters for making slices were selected: weight at 220mg per slice and pressure at 2.5t.
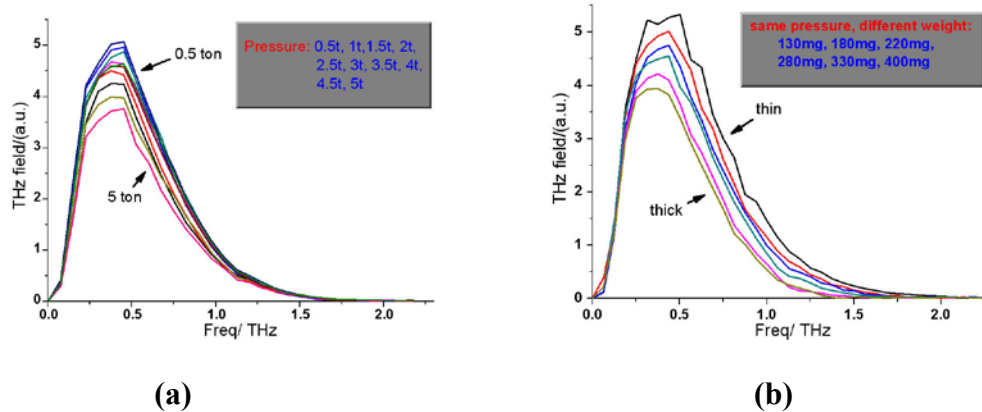
(a)   (b)

Fig. 5. THz spectra of slices under different parameters: (a) different pressure. (b) different weight per slice.

Measurement of THz spectroscopy of samples and modeling
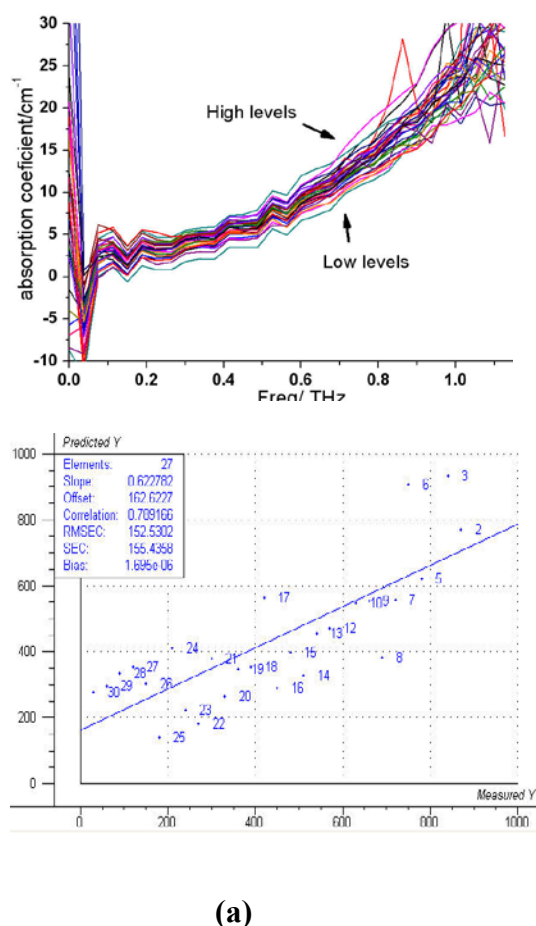

(a)   (b)

Fig. 6. Results of measurement and PLS modeling: (a) Absorption spectra of thirty samples with Pb^{2+}. (b) established PLS model for prediction.

THz absorption curves of all 30 samples were measured in Figure6 (a). Samples with different concentrations of heavy metal Pb^{2+} showed different

absorption characteristics in THz band. The spectra of thirty samples with different Pb^{2+} levels indicated that, the adsorption intensities were proportional to the difference of Pb^{2+} concentrations. The absorption increased as the Pb^{2+} concentration increased. It shows great correlation.

Algorithms such as data-smoothing methods were used to preprocess the collected data first. Multivariate statistical analysis was then conducted based on the preprocessed data. Calibration and prediction models were established based on PLS methods using the full THz wavelengths in Unscrambler software. From Figure6 (b), with the established PLS model based on leave-one-out cross-validation algorithms using the whole THz band spectroscopic data, the correlation coefficient for prediction can reach 0.62, however, the Root Mean Standard Error of Calibration (RMSEC) and Root Mean Standard Error of Prediction (RMSEP) are 152.53 and 187.68 respectively, which means the model is not so steady. Much more algorithms are required to improve this model.
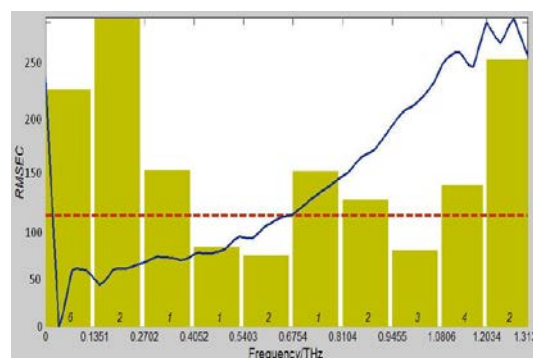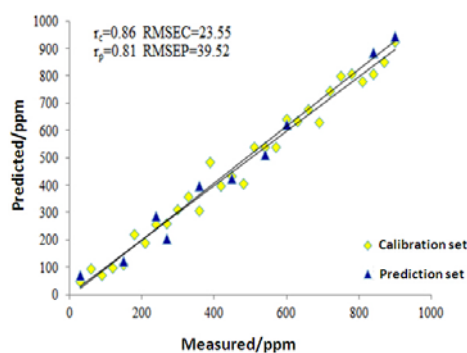
(a)   (b)

Fig. 7. i-PLS modeling and optimization: (a) i-PLS calculation. (b) established i-PLS model for prediction.

I-PLS method was then used to optimize the model. The whole THz band was divided into several sub-bands and PLS was used in each sub-band. Sub-bands which were well performed were selected and finally sensitive THz wavelengths were selected. Model was re-established using these sensitive THz wavelengths and results were shown in Figure 7(b). From the results, the

correlation coefficient for prediction can reach 0.81 and the Root Mean Standard Error of Prediction (RMSEP) is 39.52, which shows the model was greatly improved. However, considering the correlation coefficient and RMSEP values, the model is still need more improvements and much more data pre-processing algorithms are required.

CONCLUSIONS

In this paper, aiming at the server situation of heavy metals pollution, development of an advanced, safe, efficient and portable detection method for heavy metals content in soil was discussed. Experiments on soil samples with heavy metals preparation and detection using THz spectroscopy were designed and studied. Pressed-slices method for making measuring samples and suitable making parameters were determined; soil samples with different heavy metal ions were separately prepared and measured in Xiaotangshan Precision Agriculture Demo Base and Capital Normal University with THz Time-domain systems. A model based on PLS was firstly established and studied using collected preprocessed data and then optimized using i-PLS algorithm. However, more investigation on measurement principles and a large amount of sample tests are still needed to improve the detection method. Other heavy metal ions pollution detection methods still need more research.

THz is brand-new and the emitting and detecting instruments are expensive at present, however, THz equipment developed rapidly and portable equipment are emerging in the market and the price is much cheaper than before. It shows great potential in-field applications in the future. With the detection results, it can be found the heavy metal Pb^{2+} pollution special distribution information of the soil in-field and get the "pollution map". Specific measures shall be taken based on the "pollution map" to manage the soil to improve the farmland productivity. It will be a very important part of precision agriculture applications as the development of economy in future. This study will provide a reference for heavy metals pollution detection solutions for precision agriculture and sustainable agriculture development.

ACKNOWLEDGEMENTS

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