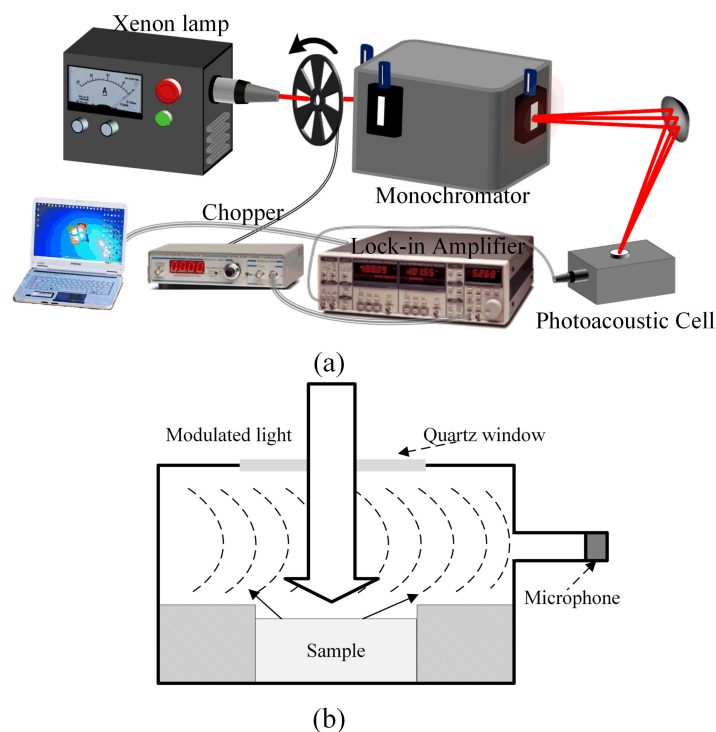


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Abstract: Heavy metal pollution in soil has severe impact on the human health and global environment. There is an urgent need for cost-effective devices capable of recognizing and detecting heavy metallic matters in soils. A broadband photoacoustic spectrometric (PAS) system was established for the detection of heavy metal contaminants in soil. The heavy metal element lead (Pb) was selected as a preferred detection target. The near infrared photoacoustic spectra of contaminated soil samples with various concentrations of Pb were collected and the spectroscopic relationship between the soil absorption peaks and Pb concentrations was analyzed. Four advanced spectral preprocessing methods were explored to improve the robustness of the prediction model. Based on the maximal correlation coefficient and minimal root mean square error criteria of prediction, a two-layer feed-forward network with a continuum removing preprocessing method with a correlation coefficient as 0.96 was tested as the most appropriate method for Pb concentration prediction. This fact verifies that the broadband PAS evaluation methodology, as a nondestructive testing method, can be potentially used as an alternative quantification detection method of heavy metal contaminants in soil without the involvement of complicated sample pretreatment.

Index Terms: Photoacoustic spectroscopy (PAS), non-destructive testing, heavy metal contamination, broadband absorbing evaluation.

1. Introduction

Heavy metal (HM) contamination, as one of the main soil pollutants, may transport from soils to plants, and have adverse effect on their growth [1]. Due to their persistent nature and long biological half-lives, elevated concentrations of HM pollutants in soil can lead to their accumulation in food chain, and eventually threaten human health [1]. By spatial distribution sampling and laboratory chemical analysis, most conventional HM detection methods (e.g., wet chemical analysis) are versatile and generally used in analyzing constituents and concentration of different HMs [2]. However, those methods may be time-consuming and require complicated sample pretreatments. Spectroscopic technology, on the other hand, is known as a non-destructive, reproducible

and environmental friendly methodology, which has the potential for simultaneous analysis of HM contamination and other soil properties [3].

Near infrared reflectance spectroscopy combined with partial least squares algorithm was introduced for HM prediction in freshwater sediments [4]. Using multiple linear regression model, a visible-near infrared reflectance spectral measurement of mining contaminated soil was reported [5]. Other studies also indicated the near infrared spectroscopy has the capability of HM contaminants calibration according to the correlation between HMs and the spectrally active constituents in soil [6]–[8] although HMs process featureless response to the infrared illumination. Regarding these foregoing spectroscopic research works, all of them were based on commercial spectroradiometers with an optical intensity over tens of watts [9], [10] which may be sophisticated and costly. There is an intrinsic conflict in common optical detectors between their sensitivity and optical response bandwidth. Some infrared detectors even require liquid nitrogen cooling and may further complicate the system.

There has been a continuing and increasing interest in photoacoustic spectrometric (PAS) evaluation methodology due to the advantages of high sensitivity, simplicity and robustness of implementation [11], [12]. PAS is ideally a zero-background technique and unaffected by light scattering since the signal is generated from incident light absorption. The acoustic sensors (e.g., microphone or tuning fork), which is completely irrelevant to optical band width, usually hundred times less costly than optical detectors. The identification of agricultural soil constituents with mid-infrared PAS yielded a larger number of features than the total reflectance spectra [13]. However, to our best knowledge, the studies for PAS methodology focusing on the estimation of HM contamination in soil are seldom reported. In this study, a broadband and cost-effective PAS system was established for the quantification evaluation of HM contaminants in soil. A typical HM element Pb was used as the case study target pollutant. A compact photoacoustic cell was designed and fabricated with only a small amount of sample needed for the experiments. This work provides an alternative and realistic approach for high performance of HM contaminants monitoring, which can assist soil property survey.

2. Experimental Details

Soil sample qualifies the standard level of Soil Environmental Background Value, and thus can be regarded as contamination free. The soil average organic matter content is 4.4%. Texture analysis shows the ingredients of the soil in this area are 45.4% clay, 34.6% sand and 35% silt on average. In order to minimize the effect of moisture in soil, all the samples were air-dried for several days at ambient temperature. After removing plant residue and stones, the samples were finely ground, sieved to 0.75 mm, and stored in brown bottles for subsequent study of soil properties. The results of the saturation paste extract in a 1: 2.5 water [14] suspension using pH meter (KEDIDA CT-6021A) showed the pH value of the soil samples was 7.8.

These soil samples were divided into 8 groups with 50 samples in each group. We chose lead nitrate ($\text{Pb}(\text{NO}_3)_2$, supplied by KESHI Co. Ltd.) as the contamination compound. The reagent was of analytical pure and diluted with distilled water. All groups of soil were sprayed with the artificial contaminant Ld in prior to simulate industrial discharge HM pollution. The soil samples with various Pb contaminated concentrations were prepared. The descriptive statistics are shown in Table 1.

The PAS configuration based on a broadband source was depicted in Fig. 1(a) [15]. A Xenon lamp (estimated total optical intensity: 2 W) was used as the illumination source which is mounted on a tripod. The beam propagated through a monochromator for the optical wavelength scan. The monochromatic light was modulated by a 50% square-wave duty cycle chopper and directed vertically into the homemade photoacoustic cell as shown in Fig. 1(b). The chamber volume is about 0.63 cm^3 , with only 1.7 g soil sample content for one concentration set of photoacoustic measurement. The modulation frequency was chosen as 80 Hz. The photoacoustic signal was detected by a BSWA Tech MPA201 electronic condenser microphone the sensitivity of which is 51.3 mV/Pa. For the protection of the acoustic sensor, a thin tube was used to bridge the chamber and the microphone. The output signal of the lock-in amplifier was collected and stored by a laptop.

TABLE 1
Descriptive Statistics of Soil Samples

Group	1	2	3	4	5	6	7	8
Mean ($\mu\text{g/g}$)	5.1	53.8	203.1	297.9	802.0	1243.2	1542.1	2235.0
Min ($\mu\text{g/g}$)	4.6	53.2	202.5	297.6	801.7	1242.7	1541.6	2234.7
Max ($\mu\text{g/g}$)	5.3	54.5	203.4	298.3	802.3	1243.4	1542.6	2235.4
Numbers	50	50	50	50	50	50	50	50

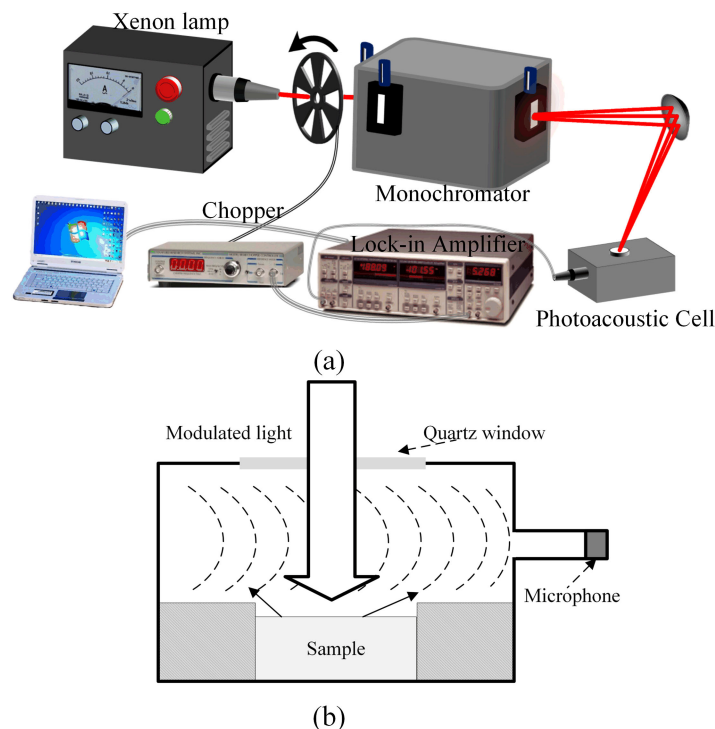


Fig. 1. (a) PAS experimental schematic. (b) The configuration of photoacoustic cell.

The photoacoustic chamber was over-filled with samples and then levelled off using a blade to ensure a flat top surface. All photoacoustic spectra were collected in the wavelength range from 800 to 2000 nm with an interval of 1 nm. The final spectrum was obtained by averaging 5 measured data to suppress random noise and increase the signal-to-noise ratio.

3. Results

The photoacoustic signal of carbon black depends only on the incident light intensity because it is a good absorber over the tested optical bandwidth and the thermal diffusion length is far greater than the optical absorption length. Therefore the absorbing spectrum of carbon black powder was used as the standard normalization reference. The photoacoustic absorption spectrum of carbon black is presented in Fig. 2(a). This curve has the identical pattern as the Xenon lamp emission

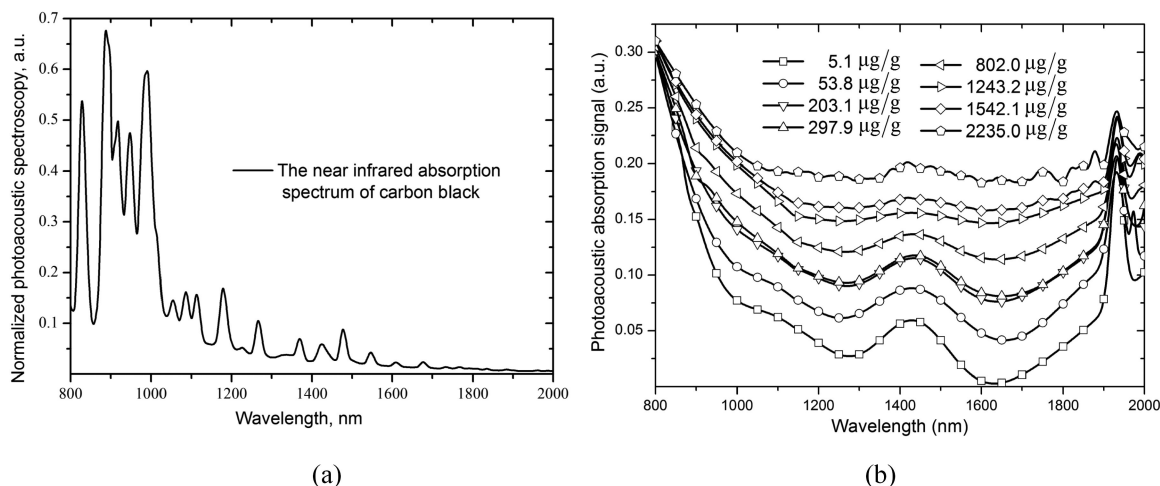


Fig. 2. (a) Photoacoustic spectrum of carbon black. (b) Photoacoustic absorption spectra of Pb contaminated soil.

characteristics shown in the product technical testing report, provides a reliable evidence for the validity of the PAS setup.

All the soil absorption spectra were normalized by the carbon black curve and selected representative spectra of different concentrations of Pb contaminated soils were depicted in Fig. 2(b). It is O-H bonds in the clay minerals and soil organic matters that significantly affect the near infrared absorption feature of the soil samples [7]. The 1400 nm absorption peak is predominantly generated by lattice O-H bonds in the hydroxyl of clay minerals [5]. The 1900 nm peak is mainly related to O-H bonds of free water [16]. Although the peaks of the characterized spectra have no direct connection to the HM element feature, they exhibit a monotonic decreasing trend towards Pb concentration which implies the possibility of quantitative evaluation of the featureless toxic HM contamination by the proposed PAS configuration.

In order to establish a reliable and robust prediction model and improve the estimation accuracy, four different pre-processing methods were implemented and discussed. Savitzky-Golay method is one of the useful smoothing algorithms for noise reduction. First derivative (FD) is effective for baseline offset removal and resolution strengthening [17]. In favor of the sharpest peaks, FD is useful to separate two or more components with overlapping spectra, nevertheless, this method may result in a deterioration in the signal to-noise ratio [18]. As a common spectral processing approach, standard normal variate (SNV) mainly eliminates the interference of solid particle size, surface scattering and the change of optical path of diffuse reflection spectra [19]. Continuum removal (CR) performs well in the enhancement of specific absorption features and the suppression of changing slope effects [20]. Regarding the fact that the existence of Pb in the samples does not add any extra or independent peaks in the absorption spectra, we used the proposed four spectral pretreatment to try to extract quantitative values from these “featureless” spectra.

After smoothing by Savitzky-Golay algorithm, the obtained absorption spectra were pre-processed with the methods of FD, SNV and CR, and the results were shown in Fig. 3(b)–(d). All approaches strengthen the absorption features around 1900 nm where the peaks become more prominent. The preprocessed spectra indicate more obviously that the absorption peaks of soil decreases as the Pb concentration rises. These spectra processed by CR algorithm was more distinguishable than the others as the absorption peaks at 1400 nm are also revealed and steepened. The rest two approaches result in either inconspicuous (FD processed) or less obvious (SNV processed) peaks at the corresponding location. It is fairly clear that the 1900 nm peak is more obvious, therefore, the photoacoustic absorption amplitude from 1600~2000 nm was used for further analysis.

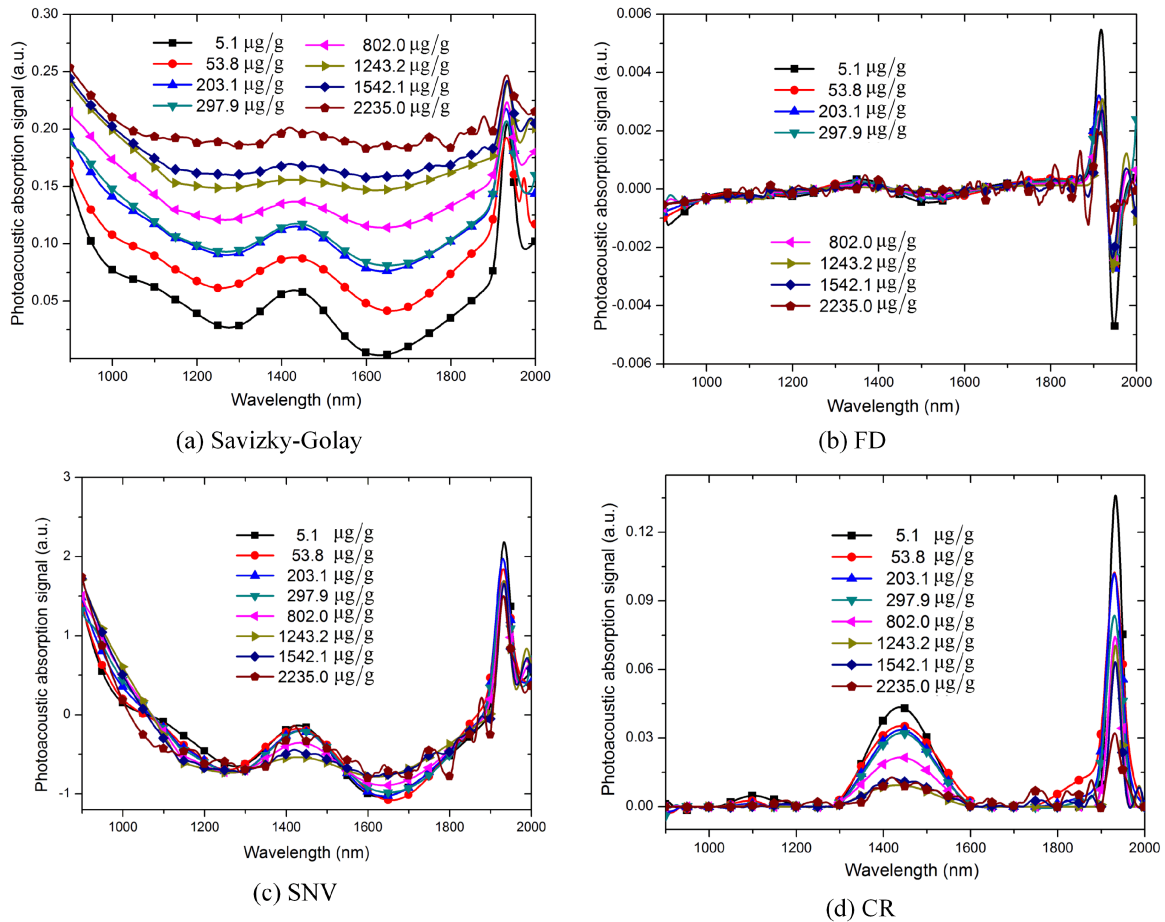


Fig. 3. Photoacoustic spectra of Pb contaminated soil preprocessed with four methods. (a) Savizky-Golay smoothing. (b) FD. (c) SNV. (d) CR.

TABLE 2
Prediction Results With a Two-Layer Feed-Forward Neural Network

	No preprocessing	SG	FD	SNV	CR
R^2	0.84	0.88	0.77	0.91	0.96
RMSEP	52.89	70.11	94.71	47.04	29.50

A two-layer feed-forward artificial neural network (ANN) was introduced for constructing the HM contamination concentration prediction model. The photoacoustic spectra from 1600 nm to 2000 nm and the Pb contamination concentration were set as the input and output of the network respectively. All the photoacoustic spectra data of the contaminated soil were set as the input and the Pb contaminant concentrations were as the output of the ANN model respectively. There were 70% data used as training set, 15% data as validation set and 15% data as testing set. As the assessment results shown in Table 2, the ANN model with the CR preprocess was verified to be the most appropriate algorithm according to the criterion of maximal correlation coefficient (R^2) and

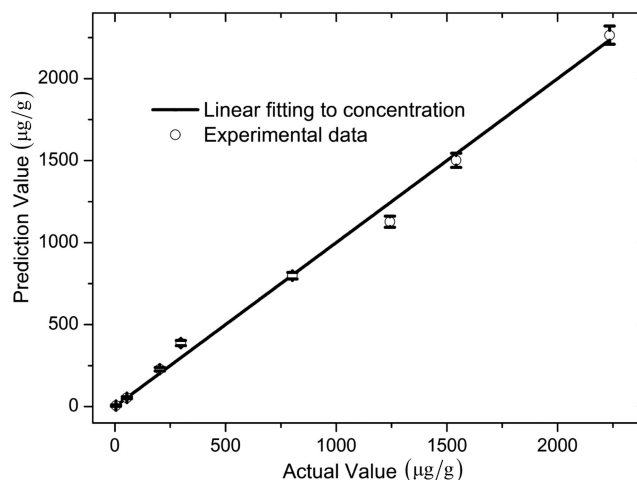


Fig. 4. Photoacoustic prediction value vs actual data.

minimal root mean square error of prediction (RMSEP) which is depicted in the following equation.

$$RMSEP = \sqrt{\sum_i^N (y_i^* - y_i)^2 / N}$$

where y_i^* is the predicted value, y_i is actual value, N is the number of soil samples. The prediction results with the CR preprocessing method was shown in Fig. 4.

The minimum experimental measurement concentration was $5 \mu\text{g/g}$ for Pb contaminant, preceding the requirement of the Chinese National Environmental Quality Standards for Soils (GB 15618-2008, the standards stipulate the safety limitation concentration for Pb is $50 \mu\text{g/g}$ for the case of soil pH > 7.5 , and the pH value of the experimental soil is 7.8). It demonstrates that the broadband, cost effective PAS system established in this research is capable for quantification analysis of HM contaminants in soil.

4. Conclusion

This study demonstrated the feasibility of applying near-infrared PAS configuration and ANN algorithm to build a reliable and quantitative spectrometric evaluation methodology for HM contamination in soil. A broadband PAS system with a small volume photoacoustic cell was designed, assembled and verified. The PAS method has the capability for the estimation of featureless toxic HM since the profiles of soil absorption spectra are affected by the HM contamination concentration. Four preprocessing approaches (Savitzky-Golay smoothing, FD, SNV, CR) were employed to improve the signal-to-noise ratio and enhance soil spectral features. The two-layer feed-forward ANN with CR method presented the best prediction results for Pb contaminant, according to the maximal R^2 (0.96) and the minimal RMSEP. In conclusion, by virtue of broadband and high sensitivity, the PAS methodology combined with ANN algorithm was verified to be an alternative approach for quantification evaluation of HM contaminants in soil.

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