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# A Portable Electrochemical workstation using Disposable Screen-Printed Carbon Electrode decorated with Multiwall Carbon Nanotube-Ionic Liquid and Bismuth Film for Cd(II) and Pb(II) Determination

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Heavy metal ions endangered human health seriously when they were absorbed and accumulated into in plants and animals. However, instruments using in labs and testing agencies were large size, expensive and complex operations, which were difficulty applying for heavy metal ions determination in situ. To solve this problem, we explored a portable electrochemical workstation and disposable screen-printed carbon electrode(SPCE), which were employed to determinate Cd(II) and Pb(II). This SPCE was modified with multi-walled carbon nanotube(MWNT) and ionic liquid(IL), and then reduced a bismuth film(BI) in situ. The characteristics of BI/MWNT-IL/SPCE were investigated through electrochemical methods including cyclic voltammetry and impedance spectroscopy. Some parameters of BI/MWNT-IL/SPCE were optimized with our portable device. By optimizing and testing, the linear relationship between peak currents and concentrations of Cd(II) and Pb(II) was established, which got the linear range from 1.0 to 60 μg/L for Cd(II) and for Pb(II) with the detection limit of 0.5 μg/L and 0.12 μg/L (S/N = 3). Finally, this portable electrochemical workstation and electrode were employed to the determination of Cd(II) and Pb(II) in soil samples with satisfactory results.

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**Keywords:** Electrochemistry, Heavy metal ion, Screen-Printed Carbon Electrode, Bismuth Film, Multiwall Carbon Nanotube, Ionic Liquid

## 1. INTRODUCTION

Unsustainable development of industry and agriculture, many activities have caused a variety of environmental problems including air, water and soil pollution in China over the past thirty years [1-3]. As for agriculture, excessive use of fertilizers and pesticides seek to maximize crop yields and the concept of sustainable development is overlooked, which have caused plenty of serious contamination in the agricultural environment, especially the soil environment [4]. Soil pollutant including cadmium, mercury, arsenic, copper, lead, chromium, zinc, nickel, DDT and polycyclic aromatic hydrocarbons are urgent to remediate[5-8]. Heavy metal ions in soil can be easily absorbed by the crops [9], and then these crops may be eaten and entered in animals and humans along with food chain[10], which can be irreversibly accumulated in organs[11-13], such as kidney, liver, lung and pancreas. If heavy metal ions excessed, it will cause some serious disease containing neurological, gastrointestinal, skeletal illnesses. Through statistic, the proportion of excellent farmland in China is only 19.4 % and the rest has been mainly contaminated by heavy metals in various degrees. Thus, it is necessary to establish a simple, rapid and inexpensive method to trace the quality and quantity of heavy metals in soil, which can provide the foundation to assess the potential risk of soil pollution.

Different analytical techniques[14] based on spectroscopic methods including UV-spectrophotometer[15], X-ray fluorescence detection[16], atomic fluorescence spectrometry[17], inductively coupled plasma mass spectrometry[18], have been developed and applied in research laboratories and professional testing institutions with high sensitivity and detection precision. However, these instruments are very expensive, great bulk, time-consuming and complex operations that are not suitable for farmer and worker to monitor heavy metals in-situ[19]. In comparison, the technique based on electrochemical method owns many special merits containing portable, simple to use, low cost and rapid detection, which overcomes the deficiency of spectroscopic methods. Over the years, almost researches are focused on exploring electrochemical electrodes for heavy metal ions detection to enhance the sensitivity and selectivity[20], which neglects to develop and improve the professional and portable electrochemical workstation. Thus, it is imperative need to develop an accurate, portable, inexpensive and easy-to-use device to evaluate heavy metal ions in the soil easily.

In this work, a portable electrochemical workstation is designed and developed for heavy metal ions detection. The hardware of this device uses accurate and reliable functional modules, such as a control unit, a potentiostat, signal conditioning circuits and a power module, which can generate the signal of square wave stripping voltammetry and collect the voltage-current signal produced by a heavy metal electrode. The related software written by C# language can set parameters, send commands, handle data and draw stripping voltammetry diagram. To improve the practicability, we need to develop a portable sensor with our portable device for heavy metal detection. A disposable screen-printed carbon electrode (SPCE) modified with multi-walled carbon nanotube (MWNT), ionic liquid (IL) and bismuth film (BI) in situ to improve the sensitivity is designed and fabricated, which is matched with the portable electrochemical workstation for Cd(II) and Pb(II) detection. The performances of BI/MWNT-IL/SPCE are investigated using some electrochemical methods. Moreover, the electroanalytical parameters using the portable electrochemical workstation and BI/MWNT-IL/SPCE are optimized and the linear relationship between peak currents and concentrations of Cd(II) and Pb(II) is established.

## 2. EXPERIMENT

### *2.1 Chemicals and reagents*

Standard solutions of Pd(II), Cd(II) and BI(III)(1000 mg/L) were purchased from National Standard Reference Materials Center of China and diluted as required. Sodium acetate-acetic acid buffer solution was selected as the supporting electrolyte for experiments. The rest of chemicals not mentioned here were of analytical reagent grade and were used as received. Multi-walled carbon nanotube was purchased from Xianfeng nanomaterials technology co., LTD (Nanjing, China). IL (N-octyl pyridinium hexafluorophosphate, Purity>99%) was obtained from Shanghai Chengjie Chemical co., LTD. Ethanol, nitric acid and sulfuric acid were purchased from Beijing Chemical factory. Double distilled water was used throughout.

The characteristic data of cyclic voltammetry and impedance spectroscopy was measured by a CHI 760C electrochemical workstation (CHI Instrument Company, Shanghai, China). The rest of measurements were collected using the portable electrochemical workstation. Flame atomic absorption spectrometer (AEEnit 700) was used for heavy metals detection in soil samples.

### *2.2 Instrument*

### *2.2.1 Principle*

Square wave stripping voltammetry, one of anodic stripping voltammetry, owned high sensitivity for the quantitative determination of specific ionic species, which need a three-electrode system and contained two main steps. For the deposition step, a working electrode was maintained at a cathodic potential that was low enough to reduce the heavy metal ions for a certain time, so that heavy metal ions can move and deposit on the working electrode surface. After that, raising the working electrode to a higher potential and striping the heavy metal ions. As the heavy metal ions were reduced, they given off electrons that were measured as a current. Due to different stripping potential among different metal ions, it was easy to identify the type of heavy metals.

### *2.2.2 Hardware*

As shown in Figure 1, the hardware was mainly consisted by functional modules, such as MSP430 MCU, potentiostat circuit, I/V converter circuit, filter circuit, serial communication circuit and auxiliary circuits. It can generate an electric signal of square wave stripping voltammetry, collect voltage values and corresponding current signals, process the signal and transmit the result to upper computer. Here, the MSP430F169 chip was chosen as the control core of the whole hardware platform, which was produced by Texas Instruments (TI) company. It was a new ultralow-power MCU consisting of different sets of modules targeted to various applications, which had been widely used in low-power and portable instrument to achieve the generation of electrochemical excitation signal and the processing and transmission of data. The hardware controlled by the MSP430F169 chip can fulfill processes of enrichment, scanning, cleaning and analysis automatically in electrochemical analysis. Its output voltage was ranging from -3 V to +3V with an accuracy of 0.1 % and resolution of ＜1 mV. The current acquisition range was ±10 mA with an accuracy of 0.1% and the minimum resolution of 10 pA. With the human-computer interaction advantage of Microsoft device, professional and fast detection mode which could meet the needs of professional and ordinary users respectively were developed to simplify the complex process of electrochemical detection and analysis.

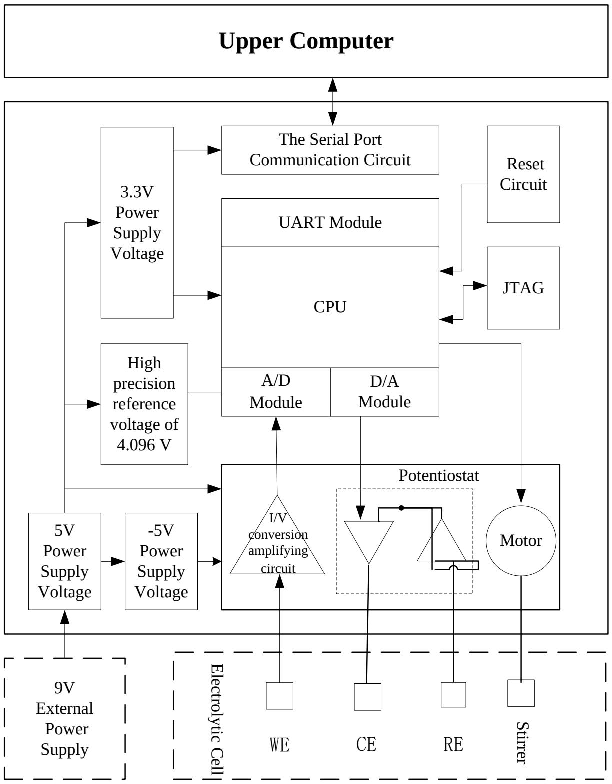

**Figure 1.** The overall structure

Three electrodes were employed to collect voltage-current signal in an electrolytic cell. BI/MWNT-IL/SPCE as working electrode can enrich heavy metal ions on its surface and reduce heavy metal ions to heavy metal atom. A platinum wire as counter electrode is used to flow the current and measure the current value and an Ag/AgCl as reference electrode is used to ensure the potential of the working electrode. A magnetic stirrer was used to stir the solution in the electrolytic cell during the deposition steps.

### *2.2.3 Software*

The software was developed in Visual Studio, which included login interface design and program design. The main program using C# language development realized the functions such as communications link, parameter settings, data collection, data mapping and spectrogram analysis. To communicate the upper computer with the hardware, selected USB port to which the instrument is connected and clicked “connect” button. Then default parameters were set up automatically. Finally, clicked “start” button on the interface and the voltage and current data will be displayed.

### *2.3 Fabrication of MWNT-IL/SPCE*

MWNT were placed into an acid solution for 6 h that mixed concentrated $HNO_3$ and concentrated $H_2SO_4$ (V/V = 1:3). The carboxylation of MWNT were filtered and washed using double distilled water until the pH of filtrate was neutral, and then dried at 80 °C in a vacuum oven. 5 mg carboxylated-MWNTs and 2 mg IL were taken and dispersed in 10 ml ethanol through sonicated for 2 hours to form a homogeneous solution. The mixed solution of MWNT-IL was dropped on SPCE and MWNT-IL/SPCE was annealed in ambient air at 80 °C for 30 min.

### *2.4 Measurement Procedures*

To detect the Cd(II) and Pb(II) in the extract of soil sample, the square wave anodic stripping voltammetry (SWV) measurements were performed in 0.1 M acetate buffer solutions. The deposition potential of -1.2 V was first applied to the working electrode for 400 s with stirring conditions. After 10 s equilibration period, the SWV potential scan was carried out from -1.2 V to 0 V (square wave amplitude, 25 mV; potential step, 5 mV; frequency, 25 Hz).

## **3. RESULTS AND DISCUSSION**

### *3.1 The characteristic device performance*

Figure 2. shows the responses of cyclic voltammetry of the modified electrodes in the 5 mmol/L $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol/L KCl mixture solution. At bare SPCE, a weak redox peak was observed with a peak potential separation of 400 mV. After SPCE functionalized with IL and MWNT respectively, we found the redox peak currents of IL/SPCE and MWNT/SPCE increased and the peak potential separations decreased in comparison with SPCE, which can be attributed to the good conductivity of two material as well as large specific surface area of MWNT. While at MWNT-IL/SPCE, the redox peak further enhanced with a small peak potential separation of 100 mV, suggesting that the electron transfer was dramatically improved due to the complex effect of IL and MWNT.

Figure 3 shows electrochemical impedance spectra of SPCE before and after modification. The value of electron-transfer resistance was mainly affected by the electrical conductivity of electrode/electrolyte interface. The resistance of SPCE was got as 13 KΩ. While at IL/SPCE, MWNT/SPCE and MWNT-IL/SPCE, the values of resistance were 2.0 KΩ, 3.2 KΩ and 0.7 KΩ respectively, suggesting the electron-transfer rate between modified electrodes and electrolyte was enhanced. This results were consistent with results from the CV.

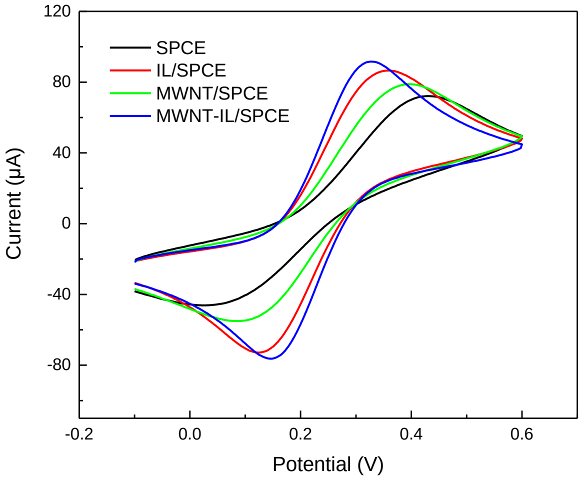

**Figure 2.** Cyclic voltammograms of (a)SPCE, (b)IL/SPCE, (c)MWNT/SPCE and (d)MWNT-IL/SPCE with scan rate 100 mV/s in 5 mmol/L $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol/L KCl;

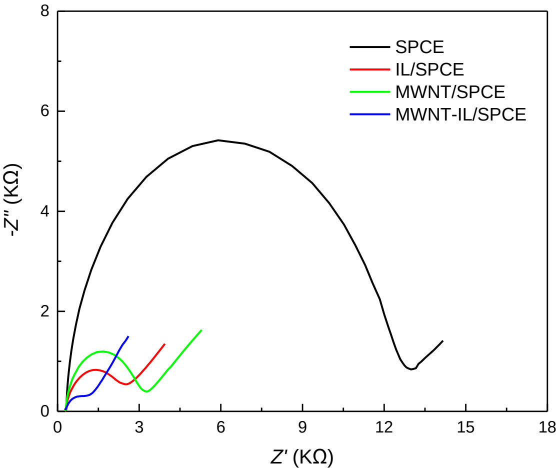

**Figure 3.** Electrochemical impedance spectra of (a)SPCE, (b)IL/SPCE, (c)MWNT/SPCE and (d)MWNT-IL/SPCE with the frequencies from 1 to $10^5$ Hz in 5 mmol/L $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol/L KCl

Figure 4 shows potential window of MWNT-IL/SPCE before and after functionalized bismuth film in sodium acetate buffer. The MWNT-IL/SPCE without bismuth film had a relative positive hydrogen overvoltage potential about -1.2 V. After functionalized with bismuth film, the BI/MWNT-IL/SPCE displayed a more negative hydrogen evolution potential about -1.4 V, which can ascribe to the special crystal plane structure of bismuth film was less prone to hydrogen evolution.

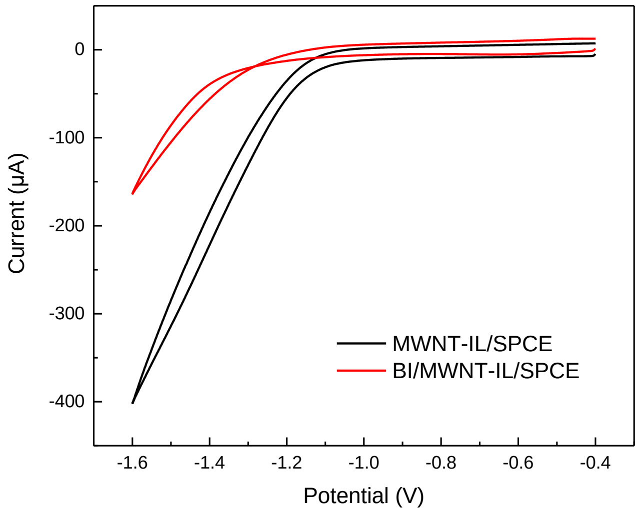

**Figure 4.** Cyclic voltammograms of (a)MWNT-IL/SPCE and (b)BI/MWNT-IL/SPCE in 0.1 mol/L acetate buffer solution

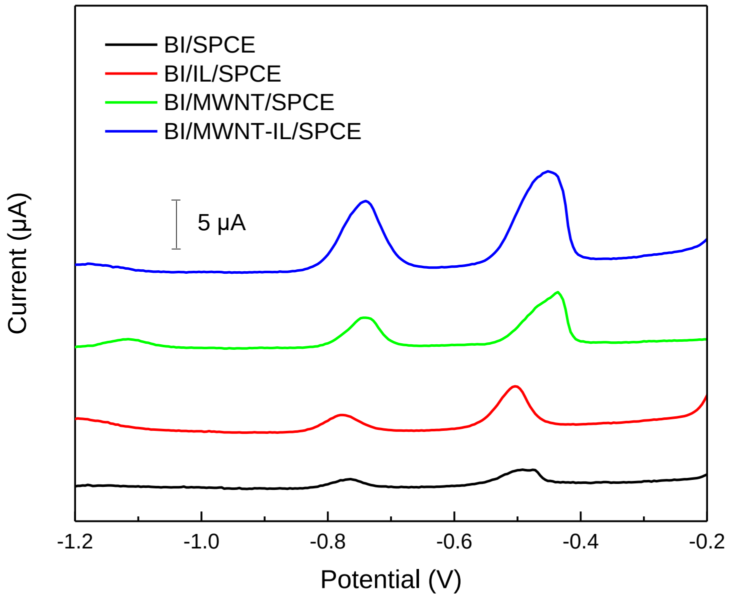

**Figure 5.** Square wave stripping voltammetric responses of 30 µg/L Cd(II) and Pb(II) in 0.1 mol/L acetate buffer solution on (a)BI/SPCE, (b)BI/IL/SPCE, (c)BI/MWNT/SPCE and (d)BI/MWNT-IL/SPCE.

Figure 5 shows the stripping responses on the different modified electrodes in 0.1 mol/L acetate buffer solution containing 30 µg/L Cd(II) and Pb(II). Two small peak currents on the BI/SPCE were observed at -0.75 V and -0.5 V, which presents the reductive peak current of Cd(II) and Pb(II). However, BI/IL/SPCE, BI/MWNT/SPCE exhibited higher stripping responses toward Cd(II) and Pb(II) because the electron transfer rate of these modified electrodes was improved greatly. The strongest peak currents were observed on BI/MWNT-IL/SPCE. The possible reason was the excellent conductivity and large specific surface area of MWNT-IL.

### *3.2 Optimization of experimental parameters*

Some electrochemical parameters using the portable device and BI/MWNT-IL/SPCE were optimized in 0.1 mol/L acetate buffer solution containing 40 µg/L Cd(II) and Pb(II).

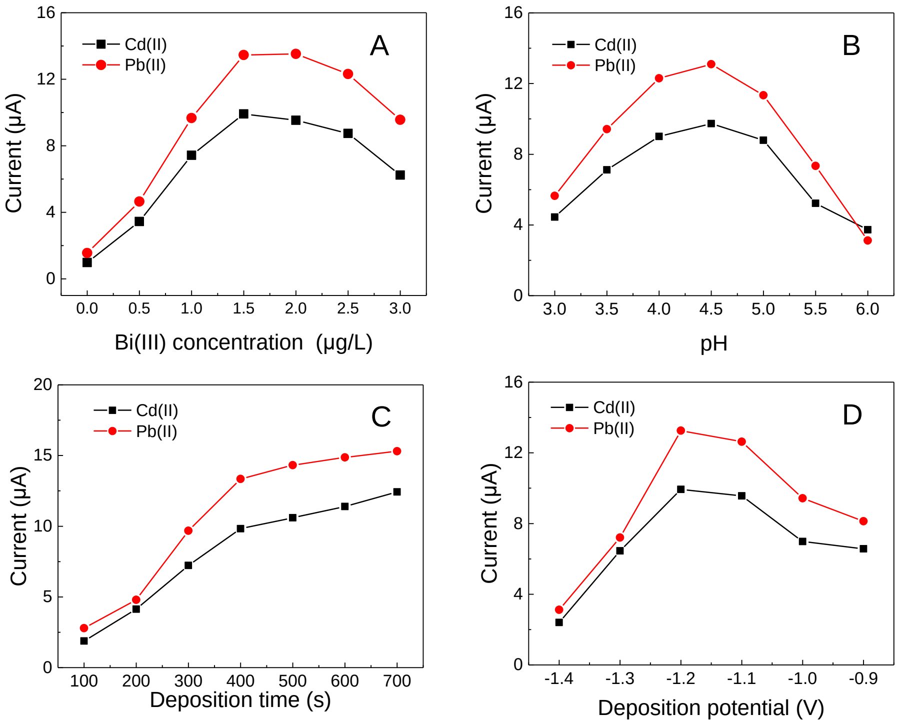

**Figure 6.** Effect of (a)Bi(III) concentration, (b)pH value, (c)deposition time and (d)deposition potential on the stripping peak current of 40 µg/L Cd(II) and Pb(II) on BI/MWNT-IL/SPCE.

Figure 6(A) shows the relationship between stripping response of Cd(II) and Pb(II) and bismuth concentration. The stripping responses of Cd(II) and Pb(II) were increased with the Bi(III) concentration from 0 to 1.5 mg/L. While the Bi(III) concentration excessed 1.5 mg/L, the stripping responses decreased. Hence, 1.5 mg/L Bi(III) was selected for further use.

Figure 6(B) represents the stripping response of Cd(II) and Pb(II) were significantly affected by pH value. The highest stripping response of Cd(II) and Pb(II) were observed at pH 4.5. The main reason is that hydrogen generated at the interface can easily damage the stability of the bismuth film if the acidity was high[22]. On the contrary, the stripping response decreased sharply due to the hydrolysis of Bi(III) in neutral media [23]. Therefore, pH 4.5 was chosen for further study.

Figure 6(C) appears the stripping response of Cd(II) and Pb(II) were influenced by the deposition time. The stripping response improved significantly with the deposition time ranging from 0 to 400 s. When the deposition time exceeded 400 s, the peak currents increased slowly. Given sensitivity and determination time, 400 s was selected as deposition time.

Figure 6(D) shows the stripping response of Cd(II) and Pb(II) are effected by the deposition potential. The stripping response of Cd (II) and Pb (II) increased gradually with the deposition potential shifted from -0.9 to -1.2 V and reduced remarkably when the deposition potential became more negative, which probably due to hydrogen evolution was occurred at such potentials. Therefore, the deposition potential performed at -1.2 V.

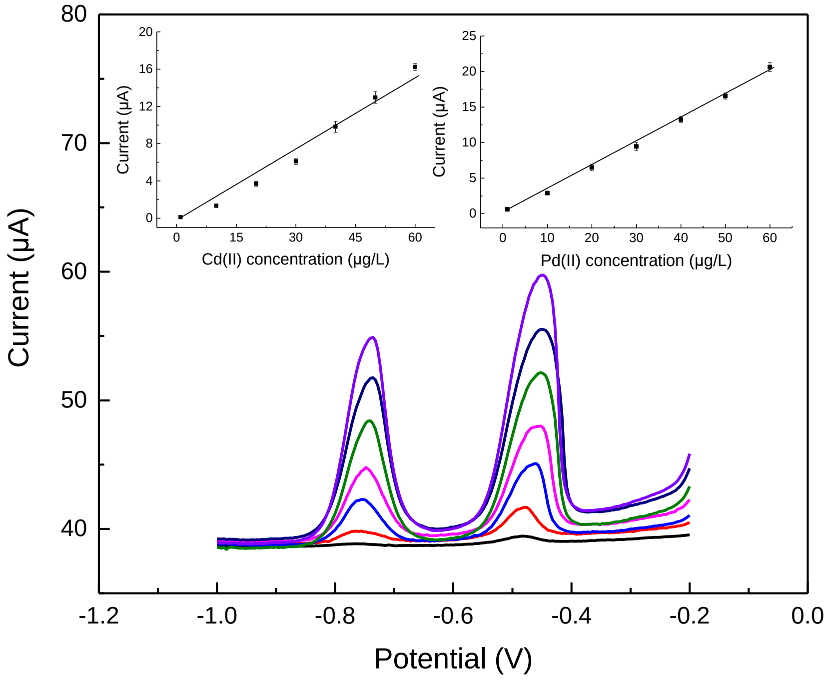

**Figure 7.** The square wave anodic stripping voltammetry for different concentrations of Cd(II) and Pb(II)

The square wave anodic stripping voltammetry was applied to determinate Cd(II) and Pb(II) using the BI/MWNT-IL/SPCE. Under the optimized conditions, a series of stripping voltammetric responses for different concentrations of Cd(II) and Pb(II) was shown in Figure 7. It was obvious that the peak currents of Cd(II) and Pb(II) were linear with the concentration of Cd(II) and Pb(II) in the range from 1 to 60 µg/L, which were revealed in insert the Figure 7. The linear regression equations were: $I$(µA) =-0.245+0. 258$C$ ($C$: µg/L) and $I$(µA) =0.263+0.34$C$ ($C$: µg/L) with the linear correlation coefficients of 0.998 and 0.997. Based on three times the standard deviation of the baseline (S/N = 3), the limit of detection was estimated to be 0.5 µg/L for Cd (II) and 0.12 µg/L for Pb(II). Compared with heavy metal electrodes reported by other groups, linear detection range and detection limit of Cd(II) and Pb(III) were summarized and listed in Table 1. It was found that the detection limit of BI/MWNT-

IL/SPCE was higher than most modified electrodes. But the lower value of linear detection range was not worse and the linear detection range can almost cover the variation range of heavy metals in soil.

**Table 1.** Comparison of performances of different electrodes for Cd(II) and Pb(II) detection

| Electrodes | Liner range (μg/L) | | Limit of detection (μg/L) | | References |
|---|---|---|---|---|---|
| | Cd(II) | Pb(II) | Cd(II) | Pb(II) | |
| BO-SPE | 10-150 | 10-150 | 5 | 10 | [24] |
| Bi/NA/AG/GCE | 5-100 | 5-100 | 0.07 | 0.05 | [23] |
| GO (ERGO)–TH/GCE | 1-40 | 1-40 | 0.05 | 0.1 | [25] |
| RGO-N/Si | 5-30 | 4.1-24.5 | 0.18 | 0.03 | [26] |
| Bi/OMC-MW/GCPE | 0.5-40 | 0.5-40 | 0.1 | 0.1 | [27] |
| NF/G/PANI | 1-300 | 1-300 | 0.1 | 0.1 | [28] |
| BI/MWNT-IL/SPCE | 1-60 | 1-60 | 0.5 | 0.12 | This work |

*3.3 Interference effects*

The property of anti-interference by coexisting ions in soil was important for electrochemical detection, which was evaluated by adding various ions into standard solution containing 20 μg/L Cd(II) and Pb(II). It was found that 1-100 folds K(I), Na(I), Co(II), Ca(II), Mg(II), Fe(III), Al(III), Ni(II), $CH_3COO$(I), Cl(I), $SO_4$(II) and $NO_3$(I) did not interfere with Cd(II) and Pb(II) determination. However, Cu(II) was found to have an influence on the stripping response.

*3.4 Application to real sample analysis*

To evaluate the applicability of portable electrochemical workstation and BI/MWNT-IL/SPCE, they were employed to determine Cd(II) and Pb(II) in various soil samples.

**Table 2.** Results for the determination of Cd(II) and Pb(II) in various soil samples (N = 3).

| Sample | Add (mg/kg) | SWASV Found $^a$ (mg/kg) | | FAAS $^a$ (mg/kg) | | Recovery (%) | |
|---|---|---|---|---|---|---|---|
| | | Cd(II) | Pd(II) | Cd(II) | Pd(II) | Cd(II) | Pd(II) |
| 1 | - | 2.15±0.11 | 12.38±0.34 | 2.32±0.03 | 11.98±0.14 | 93.67 | 103.3 |
| | 5 | 7.08±0.16 | 17.84±0.41 | | | 96.72 | 105.1 |
| 2 | - | 2.47±0.15 | 19.14±0.27 | 2. 27±0.06 | 20.77±0.19 | 108.81 | 92.15 |
| | 5 | 7.84±0.27 | 24.86±0.29 | | | 107.84 | 96.47 |
| 3 | - | 1.53±0.07 | 6.65±0.21 | 1.52±0.04 | 7.09±0.11 | 100.65 | 93.94 |
| | 5 | 6.41±0.15 | 11.21±0.33 | | | 98.12 | 92.72 |
| 4 | - | 3.23±0.11 | 16.34±0.28 | 3.37±0.09 | 16.21±0.16 | 95.85 | 100.80 |
| | 5 | 8.15±0.19 | 20.55±0.30 | | | 97.37 | 96.88 |

a. SWASV and FAAS measurements were repeated three times (n=3)

All of the soil samples were obtained from a local farmland in the suburbs of Beijing where was not far away from a country road. The pretreatment procedures of soil were performed as follows. Firstly, a soil sample was heated in an oven at 200 °C for some time until dried completely. Then the dried soil was ground by soil lapping machine at 500 r/min for 10 min using a carnelian grinding disc. Weighting 3 g of soil sample and measuring 30 mL of 0.1 mol/L hydrochloric acid were mixed in an extraction tube and extracted heavy metal ions by ultrasonic apparatus for 30 min at room temperature. Also, the aqueous phase was filtered through a membrane. After these processes mentioned above, the pH of the extract solutions was adjusted by 0.1 mol/L acetate buffer solution and 0.1 mol/L sodium hydroxide solution.

Cd(II) and Pb(II) in soil extractions were detected by the portable instrument and flame atomic absorption spectrometry (FAAS), and the results were listed in Tab. 2. The recoveries of Cd(II) and Pb(II) in soil extractions were ranged from 92.15 to 108.81% and the t-test also indicated that the results obtained by the two methods were no significant difference.

## 4. CONCLUSION

In this work, we had designed and fabricated a portable device with a related sensor (BI/MWNT-IL/SPCE) as a specific device for heavy metal ions detection. Several advantages of the proposed system should be highlighted, which holds great promise for its wide applications in soil. First, this device was characterized by its compactness, which was easy to carry and use in the field. Second, it had simple operation, save energy and convenient maintenance. Third, experimental results showed that the proposed system had excellent consistency with atomic absorption spectrometry.

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