

Short Communication

A Portable Electrochemical Detection System based on Graphene/Ionic Liquid Modified Screen-printed Electrode for the Detection of Cadmium in Soil by Square Wave Anodic Stripping Voltammetry

Guo Zhao^{1,2}, Yongsheng Si³, Hui Wang^{1,2}, Gang Liu^{1,2,*}

¹Key Lab of Modern Precision Agriculture System Integration Research, Ministry of Education of China, China Agricultural University, Beijing 100083 P.R. China

²Key Lab of Agricultural Information Acquisition Technology, Ministry of Agricultural of China, China Agricultural University, Beijing 100083 P.R. China

³Agricultural University of Hebei, Baoding 071001 P.R. China

*E-mail: pac@cau.edu.cn

Received: 21 October 2015 / Accepted: 13 November 2015 / Published: 1 December 2015

This study presents an electrochemical detection system for the detection of heavy metals in soil. The electrochemical sensor exploited a disposable screen-sprinted electrode (SPE) which was modified by ionic liquid (IL) n-octylpyridinium hexafluorophosphate (OPFP) and graphene (GR) was fabricated and used for sensitive detection of Cd (II) in soil. Based on electrochemical sensor, this system was further used for sensitive detection of trace cadmium ions by square wave anodic stripping voltammetry (SWASV). We integrated electrochemical sensor and signal detection circuit to fabricate heavy metals detection instrument which generating square wave signal and realizing signal acquisition and processing. The sensor, detection instrument and upper computer together make up the detection system. These data signal got from detection instrument were sent to the upper computer with serial communication and further processed and analyzed by upper computer and then get the stripping voltammetry curve of cadmium ions. The heavy metal types and concentration could be got from the stripping peak potential and peak current value, respectively. The results of performance evaluation showed that this detection system could realize the detection of Cd (II) in soil on-site with automatic signal acquisition, processing and detection results displaying which was low-cost and timesaving, the linear response was observed in the range from 5.0 to 70.0 μgL^{-1} with a detection limit of 3 μgL^{-1} .

Keywords: Electrochemical sensor, Heavy metals detection, Detection system, Soil, Square wave anodic stripping voltammetry

1. INTRODUCTION

In present era, heavy metal pollution is rapidly increasing which present many environmental problems. Among all soil contamination, heavy metals are mainly accumulated in soil and are transferred to food chain through plants grown on these soils [1]. Organic pollutants could be decomposed into harmless substances by microbial degradation of organic matter and some biological or chemical processes [2]. Moreover, heavy metal is highly concerned since it bio accumulates in the environment and is non-biodegradable. The presence of heavy metals would cause existence of potential toxicity. Soil contaminated by heavy metals would cause severe threat to the environment such as crop growth, human health and food safety [3, 4]. On top of that, recent studies have demonstrated that heavy metal exposure can lead to psychotic disorders and debilitating diseases that can cause irreversible changes in human [5].

Soil contamination is indeed considered one of the main threats to agricultural soil [6]. This contamination originates from natural sources by means of mineral dissociation, weathering of parent material and atmospheric deposition as well as anthropogenic sources. Heavy metal pollution sources are also derived from industrial emissions such as waste water, waste gas and waste residue. In addition, the use of chemical fertilizers, pesticides and sewage sludge would also lead to heavy metals pollution in the soil [7]. Heavy metals like cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), manganese (Mn) and zinc (Zn) contribute the major share of soil contamination [8]. Heavy metal can enter human body through three routes, namely ingestion, inhalation and dermal contact, with crops ingestion as the main route of heavy metal exposure to human [2].

Cd is classified as one of most serious environmental contaminants by the US Environmental Protection Agency due to its wide emission and highly toxic to human [9]. Although heavy metal content is still under the permissible level, detection methods are needed since heavy metal accumulates continuously in soils and may directly damage agricultural crops and consequently affect livestock and humans via food chain process [10].

Spectroscopical (AAS, AES, ICP-MS, etc.) and electrochemical (ISE, polarography, etc.) methods were two common methods for heavy metals detection [11, 12]. These methods could realize the accurate and sensitive detection of heavy metals, but the detection process was slow and complex, the detection cost is high and the operation was needed in the laboratory environment [13]. The assessment of potential heavy metal pollution in certain region by traditional laboratory methods required a large number of soil samples and the detection process needed operate in specific environment [14]. Detection date need to be analyzed by trained personnel, which was time-consuming and inconvenient. Therefore, the shortcomings of traditional detection methods have limited their on-site detection and field application. A portable detection system could be developed for the detection of heavy metals in soil samples in the field which would save more detection time and cost.

Considering the purpose of heavy metals on-site detection and field application, an electrochemical detection system with a portable detection instrument and upper computer for heavy metals detection was developed to replace large-scale analysis instruments which are generally complicated to use, expensive and time-consuming [15, 16].

2. ELECTROCHEMICAL DETECTION SYSTEM

The system's architecture can be divided in three parts, as it can be seen in Fig.1. The prototype of electrochemical detection system was shown in Fig.2. The proposed electrochemical detection system consists of sensor, detection instrument and control platform. Sensor, as the signal recognition and acquisition part of this detection system has a strong influence on the detection performance. In order to improve the portability and detection performance of this detection system, a graphene/ionic liquid modified screen-printed electrode was developed. Detection instrument realize the processing and analysis of detection signal get from the sensor and trigger square wave signal. After the processing of the signal, the detection signal would be sent to the control platform for secondary processing. Control platform received detection information from detection instrument based on the serial communication module and the detection information would be stored in the database at the same time. The whole detection process was controlled by the control platform and the control platform was called the upper computer in this paper.

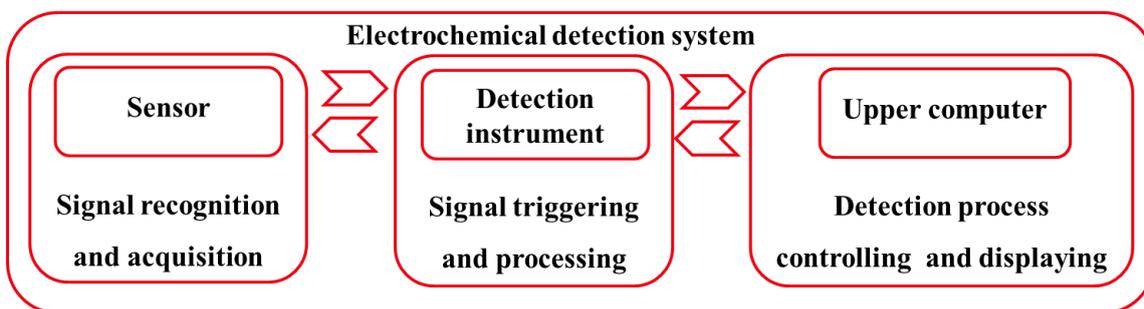


Figure 1. Structural schematic diagram of electrochemical detection system

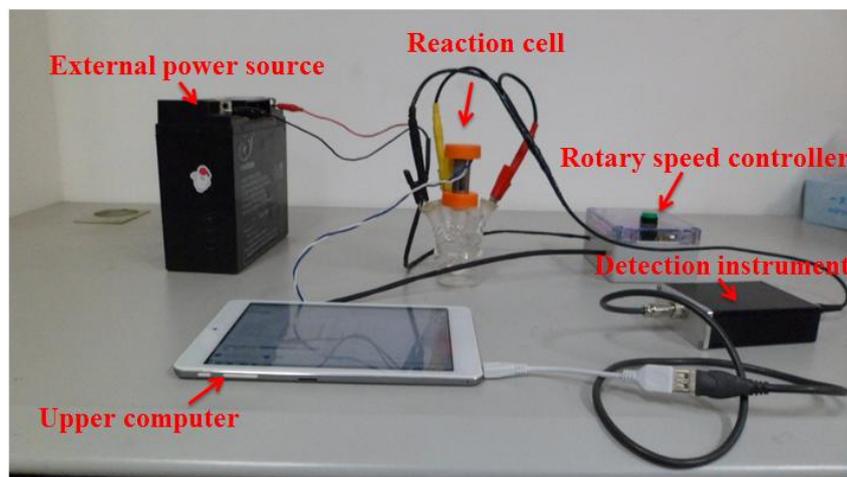


Figure 2. The prototype of electrochemical detection system

2.1 Electrochemical sensor

In order to increase detecting accuracy and portability of the proposed electrochemical detection system, a graphene/ionic liquid modified screen-printed electrode (Fig.3) were developed in

this system as a special sensor for detection instrument. The disposable screen-printed electrode has a great advantage over the mercury drop electrode [17].

In recent years, the screen printing electrode as a kind of disposable electrode have been greatly improved in both the form and printing materials. Thus, SPEs have been successfully applied for on-site detection of heavy metals in a wide range of sample matrixes due to their advantageous material properties, such as disposability, simplicity, and rapid responses. Comparing with the common hanging mercury drop electrodes, apart from the difference in size and cost, the screen-printed electrode had great advantages because they were nontoxic. In particular, the development of electrochemical sensors based on SPEs for heavy metals analysis has received massive consideration since they enable the rapid screening of the heavy metal pollution in complex matrixes, requiring small volumes of samples and no pre-treatment steps [18]. Electrochemical sensor use three-electrode system which is composed of reference electrode (RE), working electrode (WE) and counter electrode (CE).

Screen-printing electrode in the application of electrochemical detection system development had greatly improved the accuracy and portability of the detection system. Rapid detection of heavy metals in soil can be realized by this detection system based on a graphene/ionic liquid modified screen-printed electrode at a low cost.

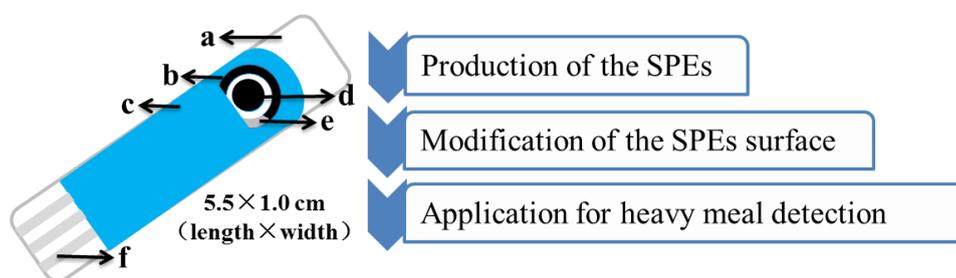


Figure 3. Development steps and representation of a SPE. (a) inert solid substrate; (b) counter electrode; (c) insulator layer reference; (d) working electrode; (e) electrode; (f) conducting paths.

2.2 Detection instrument of heavy metals

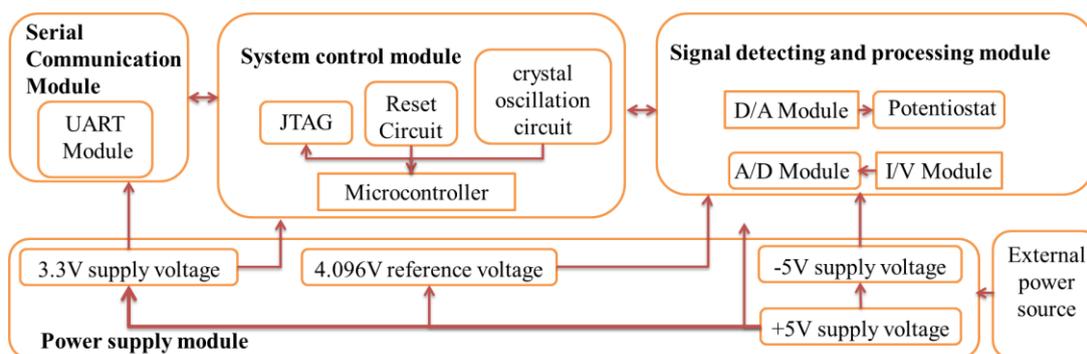


Figure 4. Block diagram of the detection instrument

The detection instrument of this electrochemical detection system was made up of signal detecting and processing module based on electrochemical sensor, system control module, power supply module and serial communication module. A block diagram of detection instrument is shown in Fig.4. The microcontroller (8 bit) played an important role in triggering square wave signal, signal processing and I/O units controlling.

This electrochemical detection system realized the heavy metals detection by square wave anodic stripping voltammetry (SWASV). This system had a good detection limit because of having an enhanced signal-to-noise ratio and the signal-to-noise ratio would be improved by enhancing analytical (Faradaic) current and eliminating background signal (Charging) simultaneously. The concentrations of heavy metals were obtained by anodic stripping voltammetry curves, this anodic stripping voltammetry curves got from the square wave excitation potential and respective current response as shown in Fig.5. The excitation potential was digital signal which generated by the microcontroller ADUC842BS62-5, the analogue signal would sent to the upper computer after converting digital signal to analogue form using a digital to analogue converter (12-bit). Working electrode and reference electrode were controlled by a potentiostat to get applied potential. At the same time, the signal output by the working electrode in the form of current which forming a closed loop with the counter electrode in solution.

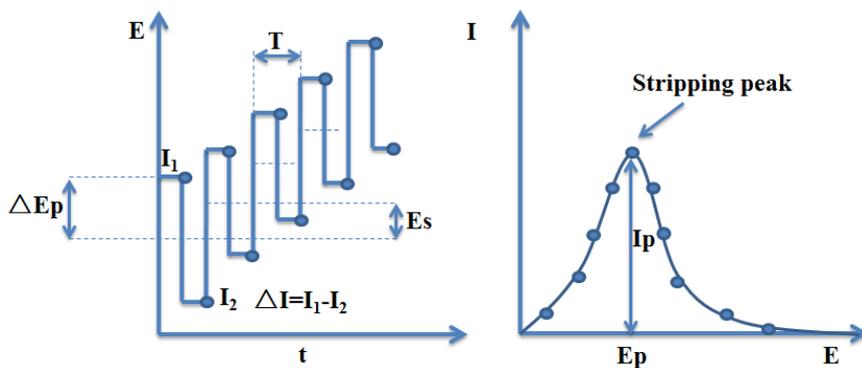


Figure 5. Schematic diagram of SWASV and its current response. Symbol meanings: ΔE_p (single channel pulse height), E_s (potential increment), T (pulse period), ΔI (net current), I_p (peak current), E_p (peak potential)

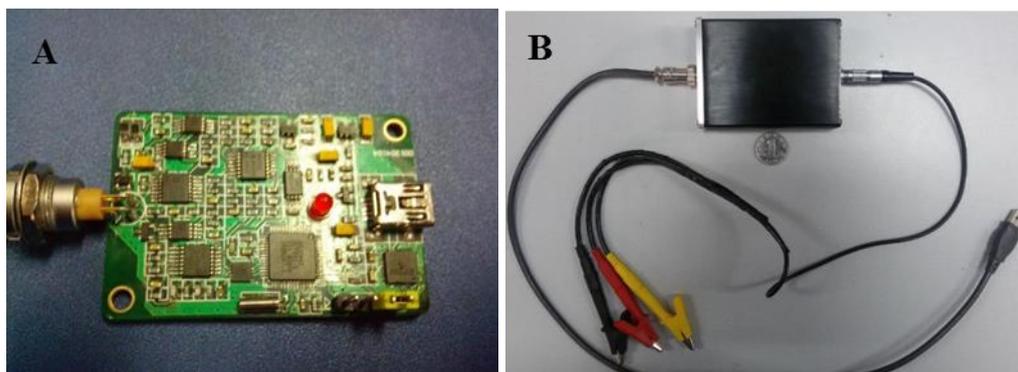
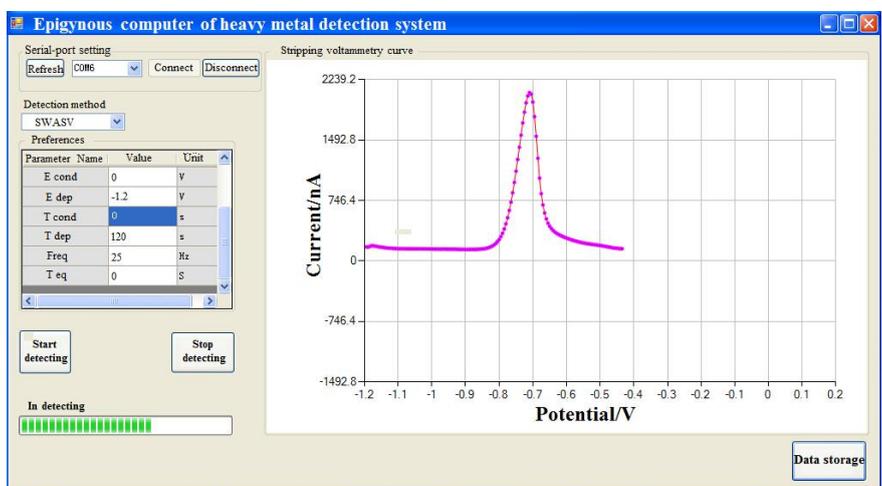


Figure 6. (A) Printed circuit board and (B) the prototype of detection instrument

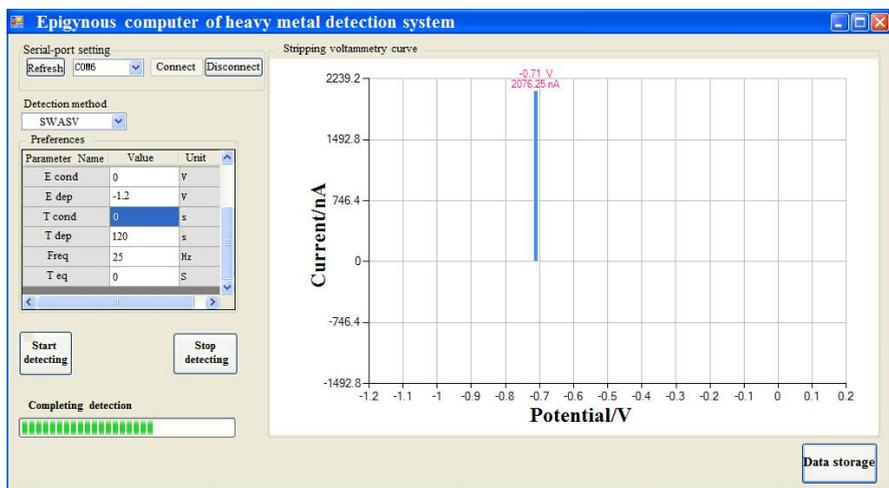
Signal detecting and processing module was developed to realize the detection and processing of the weak current signal. To achieve high-precision measurement of weak current signal, the system chose ADUC842BS62-5 as the core, including the hardware system and software system. The weak current signal was converted into voltage signal through current-to-voltage converter as an output signal. Then the voltage signal which was analog signal would be converted into digital signal by analog to digital converter (12-bit). These digital signal got from detection instrument were sent to the upper computer with serial communication and further processed and analyzed by upper computer. Microcontroller played a critical role during the data acquisition process. The printed circuit board and the prototype of detection instrument were shown in Fig.6 (A) and Fig.6 (B), respectively.

2.3 Upper computer

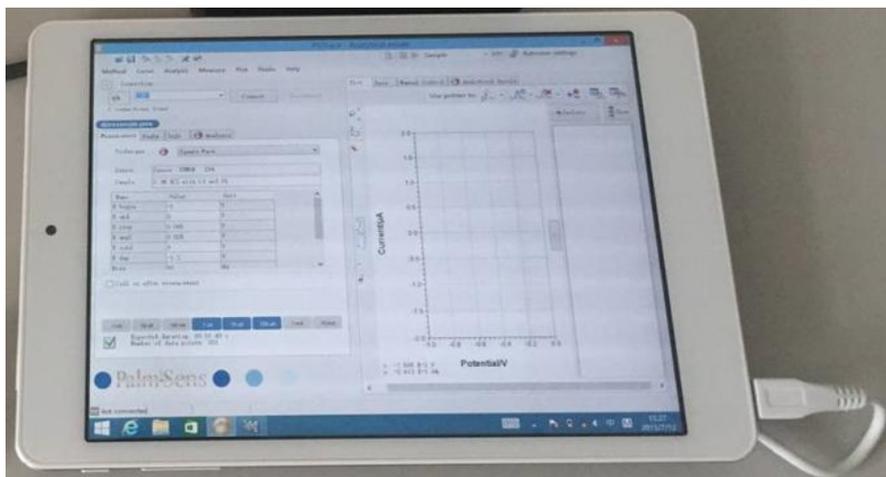
Upper computer was a tablet computer with upper computer software which was developed by C sharp programming language.



(A)



(B)



(C)

Figure 7. (A) Running Process, (B) running result and (C) the prototype of upper computer

Upper computer was designed to control detection instrument and used to realize the electro-deposition and dissolution based on detection instrument, which imitating electrochemical workstation. Further, the upper computer can realize the parameters setting, instructions sending, receiving and storing the data and drawing the stripping voltammetry curve as shown in Fig.7(A).

Detection results of heavy metals would be displayed in the form of a histogram through upper computer as shown in Fig.7(B). The user interface of the upper computer software with a single-window design which was convenient to operate. Upper computer, serving as the display and operation terminal was regarded as management and control center of the whole electrochemical detection system. The upper computer as a user interface to achieve the real-time monitoring of detection instrument and adjusting working parameters of the system such as deposition potential, desposition time and square wave frequency. More processing would be done with the data got from detection instrument in upper computer. With the electrochemical detection system, it is possible for the upper computer to receive and store data automatically. The prototype of of upper computer was shown in Fig.7(C). A convenient human-computer interaction was provided by the upper computer to realize the interaction between the detection system and the operators.

3. EXPERIMENTAL

3.1 Apparatus and reagents

Electrochemical measurements of the Cd (II) were performed on the electrochemical detection system mentioned in this paper. The working electrode was screen-printed electrode made by ourselves. A platinum wire electrode and Ag/AgCl (3 M KCl) electrode were used as auxiliary electrode and reference electrode, respectively. A 30 mL cell was used as the reaction zone for electrochemical measurements.

The commercially conductive graphite ink (Electrodag 423SS) and insulation ink (Electrodag 452SS) were obtained from Acheson Co., Ltd (USA). IL OPFP was purchased from Shanghai Chengjie Co., Ltd. (Shanghai, China). Graphite powder (spectral pure, size < 20 μ m) and cellulose acetate (CA) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). A required stock solution of Bi (III) and Cd (II) were prepared by dissolving Bi (III) and Cd (II) (1000 mg L⁻¹) from National Standard Reference Materials Center of China in ultrapure water. The 0.1 M pH 7.0 phosphate buffer solutions (PBS) were prepared by mixing the stock solutions of NaH₂PO₄ and Na₂HPO₄ to prepare the GR film. Acetate buffer solutions (0.1 M) with different pH were served as the supporting electrolyte and prepared by mixing acetic acid solution and sodium acetate solution. Millipore-Q (18.2 M Ω cm) water was used for all experiments.

3.2 Preparation and modification of GR/IL-SPE

The printing ink was prepared according to the published literature [19]. Firstly, 5 mL cyclohexane was mixed with 5 mL acetone to get their mixture. Then 0.1 g CA was added into the mixture and stirring it until CA dissolved completely. After that, 1 g OPFP and 4 g graphite powder were added to the mixture mentioned above to get composite. In order to get a viscous ink the obtained composite was sonicated for 40 min. During the process of GR/IL-SPE fabrication, the working area was formed by printing the ink made by ourselves onto the poly (vinyl chloride) (PVC) substrate. Afterwards, solvents on the electrode working area were evaporated under 80°C for 30 min. To get a circular working area (3 mm diameter), Electrodag 452SS insulating ink was used to overprint the electrode for measurements. In addition to this, ultraviolet was used to irradiate the working area for 2 h and then the epoxy resin was cured and solidified. The commercial Electrodag 423SS ink electrode was also prepared in this way for comparison. A modified Hummers method was used to synthesis graphite oxide (GO) [20, 21]. The homogeneous GO dispersions of 0.2 mg mL⁻¹ were obtained through exfoliating synthesized graphite oxide in Milli-Q water. A 6 μ L GO film was coated on the SPE surface and air-dried naturally to obtain GO/IL-SPE. GR/IL-SPE was obtained by electrochemical reduction of GO, High-purity nitrogen was passed into Na-PBS solution to avoid the oxidation of GR. The reduction process was performed at -1.2V (vs. Ag/AgCl) for 600s.

3.3 Electrochemical measurement procedure

The Cd (II) was detected by SWASV in the 0.1 M acetic acid buffer and 4.0 μ g L⁻¹ Bi (II). Electrochemical measurement procedure of Cd (II) was mainly made up of four parts: (1) deposition, (2) standing, (3) stripping and (4) cleaning. Among them, the deposition and cleaning process needed to be carried out in the state of stirring. The deposition potential of -1.2V was used during the deposition process for 120s on the working electrode. After standing for 20s, the stripping process started with SWASV potential scan from -1.2V to 0V. Before the next cycle, residual bismuth film was removed during the cleaning process at 0.3V for 30s under stirring.

3.4 Calibration curve constructing

The realization of the heavy metal detection was based on the calibration curve of peak currents and Cd (II) concentration. Under the optimized conditions, the electrochemical detection system was applied for the determination of Cd (II) by SWASV. Differential Pulse Voltammetry of Cd (II) in concentration of 5, 10, 20, 30, 40, 50, 60, and 70 μgL^{-1} as shown in Fig.8 (A). It can be seen that the peak currents exhibit a favorably linear relationship with the concentration of Cd (II) in the range from 5.0 to 70.0 μgL^{-1} . The calibration curve was calculated as $y = 0.3221x - 0.1909$ (y : μA , x : μgL^{-1}) with the correlation coefficient of 0.9975 as shown in Fig.8 (B). Based on three times the standard deviation of the blank signals ($S/N=3$), the limit of detection (LOD) was 3 μgL^{-1} with a 120s accumulation time.

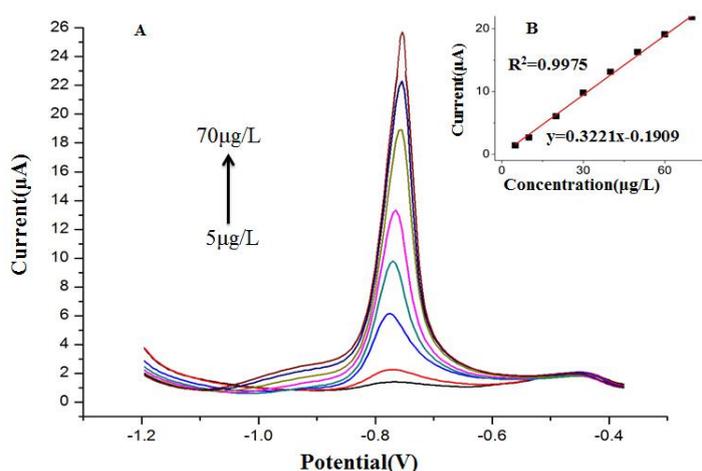


Figure 8. (A) SWASV voltammograms of Cd (II) (B) Calibration curve of peak currents and Cd (II) concentration

4. ANALYSIS OF SOIL SAMPLES

Table 1. Recovery tests and the comparison of the electrochemical detection system mentioned and AAS for the detection of Cd (II) in several soil samples.

Sample	Added (μgL^{-1})	Detection results by the proposed system (μgL^{-1}) ^a	Detection results by AAS (μgL^{-1}) ^a	Recovery (%)
1	0	3.69 ± 0.39 ^b	3.73 ± 0.02 ^b	—
	4	7.44 ± 0.33		93.75
	8	11.37 ± 0.40		96
4	0	—	1.16 ± 0.12	—
	5	5.82 ± 0.21		93.2
	10	10.93 ± 0.37		97.7
6	0	4.12 ± 0.42	4.23 ± 0.05	—
	10	13.96 ± 0.38		98.4
	15	18.92 ± 0.29		98.67

^a SWASV and AAS measurements were repeated five times ($n = 5$)

^b Mean value \pm standard deviation

In order to evaluate the detection performance in practical application of the electrochemical detection system, the concentration of Cd (II) in farmland soil samples got from the suburb of Beijing were detected by this electrochemical detection system. Owing to avoid the interference of other factors from the soil samples, the pretreatment of the soil samples was required. The detection results were verified by the atomic absorption spectrometry (AAS) method. The results (Table 1) indicated that there was no significant difference between the two techniques (relative error was less 0.45%). The feasibility of the electrochemical detection system for the detection of Cd (II) was further examined by the analysis of soil samples. The results (summarized in Table 1) showed that the electrochemical detection system using the GR/IL-SPE produced satisfactory detection results, with an average recovery of 96.29%. All of these results demonstrated that the electrochemical detection system could act as an effective method for on-site detection of Cd (II) at low (μgL^{-1}) levels in real soil samples.

5. CONCLUSION

In this study, an electrochemical detection system consists of sensor, detection instrument and upper computer to detect and identify Cd (II) in soil had been developed. This system had been developed for analysing soil samples in the field with the aim of rapid assessment of contaminated land and realizing on-site detection, which was time-saving and low-cost. The system provides those facilities designed in a traditional laboratory based professional analysis apparatus and instruments to guarantee detection performance, but in a portable design which using the tablet computer as the upper computer replaced personal computer. The identification of the heavy metals is based on chemometrics methods using a heavy metal database for data storing. The application of this electrochemical detection system has been performed on real soil samples, which was further investigated by AAS. The sensitivity of the system had been assessed and it had been found that Cd (II) could be detected at low concentrations up to $3\mu\text{gL}^{-1}$, thus indicating the performance of this system can satisfy the detection requirement of heavy metals in real soil samples. The electrochemical detection system for detection of heavy metals was also suitable for on-site detection in the field to realize rapid identification of heavy metal ions.

ACKNOWLEDGEMENTS

This work was supported by the National High Technology Research and Development Program of China (no.2011AA100704) and Research Fund for the Doctoral Program of Higher Education of China (no. 20120008110033).

References

1. M. Adrees, S. Ali and M. Rizwan, *Ecotoxicol. Environ. Saf.*, 119 (2015) 186.
2. Z. H. Cao, Z. Y. Hu, *Chemosphere*, 41 (2000) 3.
3. C. W. A. Nascimento, B. Xing, *Sci. Agric.*, 63 (2006) 299.
4. M. Adrees, S. Ali and M. Rizwan, *Environ. Sci. Pollut. Res.*, (2015)1.
5. S. Lee, B. Lee and J. Kim, *Environ. Monit. Assess.*, 119 (2006) 233.

6. X. Morvan, N. P. A. Saby and D. Arrouays, *Sci. Total Envir.*, 391 (2008)1.
7. P. C. Nagajyoti, K. D. Lee and T. V. M. Sreekanth, *Environ. Chem. Lett.*, 8 (2010) 199.
8. N. A. Omar, S. M. Praveena and A. Z. Aris, *Food Chem.*, 188 (2015)46.
9. D. J. Weiss, M. Rehkemper and R. Schoenberg, *Environ. Sci. Technol.*, 42 (2008) 655.
10. B. Wei, L. Yang, *Microchem. J.*, 94(2010) 99.
11. A. Lafaye, C. Junot and B. R. L. Gall, *Rapid Commun. Mass Spectrom.*, 17(2003) 2541.
12. K. W. Jackson, T. M. Mahmood, *Anal. Chem.*, 66 (1994) 252.
13. I. Bontidean, J. Ahlqvist and A. Mulchandani, *Biosens. Bioelectron.*, 18 (2003) 547.
14. U. Schnabel, O. Tietje, *Environ. Geol.*, 44 (2003) 893.
15. K. A. Howell, E. P. Achterberg, *TrAC, Trends Anal. Chem.*, 22 (2003) 828.
16. H. Emons, P. Ostapczuk, *Analyst*, 121 (1996) 1917.
17. G. Kefala, A. Economou and A. Voulgaropoulos, *Analyst*, 129 (2004) 1082.
18. R. A. S. Couto, J. L. F. C. Lima and M. B. Quinaz, *Int. J. Electrochem. Sci.*, 10(2015) 8738.
19. J. Ping, J. Wu and Y. Ying, *Electrochem. Commun.*, 12(2010) 1738.
20. W. S. Hummers Jr, R. E. Offeman, *J. Am. Chem. Soc.*, 80(1958) 1339.
21. N. I. Kovtyukhova, P. J. Ollivier and B. R. Martin, *Chem. Mater.*, 11(1999) 771.

© 2016 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).