

Electrochemical Characterization of Carbon Electrode in μ -Flow Sensor by On-Line Automated Flow System

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Abstract

An electrochemical anodic stripping voltammetry (ASV) coupled with auto-pretreatment system (Auto-Pret system) as an automated flow system was applied for trace metal analysis. A micro-flow sensor consisted of preconcentration membrane and three-electrode electrochemical part was used as a detector. The characterization of the carbon electrode in micro-flow sensor such as life time, reproducibility and sensitivity were performed. The micro-flow sensor was tested with 50 ppb of Cd(II) and Pb(II) in 1.0 M HCl, as a supporting electrolyte, by on-line differential pulse anodic stripping voltammetry. It was used for 160 samples with the relative standard deviation less than 10 %. Analytical parameters for quantitative determination of Cd(II) and Pb(II) were investigated by differential pulse anodic stripping voltammetry (DPASV) and square-wave anodic stripping voltammetry (SWASV). Detection limits were 2.37 ppb and 0.15 ppb for the determination of Cd(II) and Pb(II) by DPASV and 0.02 ppb and 0.01 ppb for the determination of Cd(II) and Pb(II) by SWASV. The relative standard deviation less than 8 % for Cd(II) and less than 5 % for Pb(II) were achieved with each 50 ppb of metal ion solution. The results indicated that the carbon electrode in micro-flow sensor coupled with on-line Auto-Pret system have a good efficiency for the metal ion determination.

Keywords micro-flow analysis, cadmium, lead, anodic stripping voltammetry

1. Introduction

Heavy metal ions such as lead and cadmium in the environment can be toxic to human beings, even at very low concentration [1]. Therefore, it is very important to analyze the contamination of heavy metal ions in the environmental pollution monitoring. These demands have led to increasing efforts aimed at developing new analytical tools for the simultaneous measurement of metal ions. There are several accepted analytical methods currently available for the measurement of metals in environmental samples. These include atomic absorption spectrometry (AAS) [2], electrothermal atomic absorption spectrometry (ETAAS) [3], flame atomic absorption spectrometry (FAAS) [4], and on-line micro-column preconcentration coupled with inductively coupled plasma optical emission spectrometry (ICP-OES) [5]. However, these methods require comparatively expensive equipment and they are not readily amenable to portable instrumentation. Electrochemical stripping analyses have the potential to overcome some of the problem experience by spectroscopic techniques. These techniques provide the sensitivity needed for measuring trace metals. Stripping voltammetry has been adapted to flow system with the advantages conferred by on-line analysis that provide lower sample consumption and on-line mixing of sample and reagents [6,7]. The automated flow systems with highly sensitive detection were tried to develop because of time-saving especially in sample preconcentration step, convenience for field analysis, as well as reducing sample, solvents and reagents consumption. Most of the interest in these devices arises from the potential of incorporating sample-

processing steps, such as sample pretreatment, dilution, calibration, separation, derivatization, and detection onto a cm-dimensioned “chip” [8].

In this work, we report the use of carbon electrode in micro-flow sensor for on-line electrochemical analyses. The micro-flow sensor consisted of two parts; a mini-disk membrane for sample preconcentration and three electrodes for electrochemical detection. Samples and other solutions were sequentially kept in a holding coil in the micro-flow sensor, and then moved through the detection part of micro-flow. The aim of this work is to introduce a new analytical tool for metal ion determination.

2. Experimental

2.1 Reagents and solutions

All reagents and solutions were prepared with ultrapure water (18 M Ω cm⁻¹ resistivity) obtained from an Elix-3/Milli-Q water system (Nihon Millipore, Tokyo, Japan). Cd(II) and Pb(II) working standard solutions were prepared once a week by appropriate dilution of stock standard solutions (1000 ppm, Wako Pure Chemicals, Osaka, Japan) with a 1.0 M HCl solution. A 1.0 M HCl solution, served as a supporting electrolyte, was prepared from 35% HCl (electronic grade, Kanto Chemical, Tokyo, Japan). A cleaning solution, 0.5 M HNO₃, was prepared from 69 % v/v HNO₃ (Wako Pure Chemicals, Osaka, Japan). Potassium chloride (reagent grade, Kanto Chemical, Tokyo, Japan) was used to prepare 0.1 M KCl solution.

2.2 Apparatus

Voltammograms were obtained using the PalmSens portable potentiostat (Palm Instruments BV, The Netherland). The micro-flow sensor system (Sekisui Chemical, Kyoto) consisted

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of a Ag/AgCl paste reference electrode, a carbon working electrode and a carbon counter electrode. The sequential injection analysis (SIA) system was computer-controlled with a program written by Visual Basic software.

2.3 Procedures

The micro-flow sensor was connected to the SIA system and potentiostat as shown in Figure 1. The performance of the on-line method was tested with Cd(II) and Pb(II) standard solution before apply to real samples. The on-line operating step and time necessary for the determination of Cd(II) and Pb(II) is listed in Table 1. Before use, the reference electrode was filled with 0.1 M KCl solution. The carbon working electrode of the micro-flow sensor was washed with water and conditioned with 1.0 M HCl supporting electrolyte at -1.40 V for 300 s to obtain

stable background current. Anodic stripping voltammetric measurements were performed with a bare carbon electrode in a solution of 1.0 M HCl containing 50 ppb Cd(II) and Pb(II) and applying a deposition potential of -1.40 V (unless otherwise stated) for a defined period of time (usually 180 s) under flowing conditions. Following the deposition step, the flowing was stopped for 10 s. The voltammogram was recorded by applying a positive going voltammetric potential scan. The scan was terminated at +0.80 V. Prior to each measurement, one “cleaning” scan from -1.40 to +0.80 V was performed without the deposition step, followed by a 10 s conditioning step (with flowing 0.5 M HNO₃ solution) at +0.80 V in order to clean and remove the target metals from the electrode surface. All experiments were performed at room temperature with untreated carbon electrode.

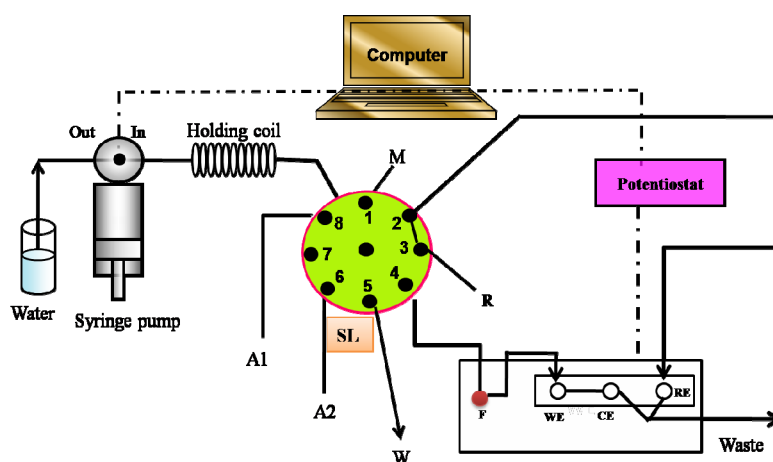


Fig. 1 Schematic diagram of instrument set up for the determination of metal ions by on-line anodic stripping voltammetry on micro-flow sensor. A1 = 0.5 M HNO₃; A2 = 1.0 M HCl; R = 0.1 M KCl; M = Metal ion solution; F = pre-concentration membrane; and W = waste.

Table 1 Step sequence and time necessary for each step

Step	Methodology	Time per 1 step
A. Filling the line	Fill the solution into tubing in SIA system	150 s
B. Sensor washing: H ₂ O	Wash the sensor with water	150 s
C. Sensor washing: Acid	Wash sensor with 0.5 M HNO ₃ and 1.0 M HCl	215 s
D. Electrode filling	Fill 0.1 M KCl for reference electrode	66 s
E. Electrode conditioning	Conditioning the carbon electrode with 1.0 M HCl for 300 s	300s
F. Background analysis	Anodic stripping voltammetric determination of supporting electrolyte, 1.0 M HCl, 3-5 times or until the background current was stable.	684 s
G. Sample analysis	Cd(II) and Pb(II) determination	684 s
H. Electrode cleaning	Wash sensor with 0.5 M HNO ₃ and 1.0 M HCl	215 s

3. Results and discussion

In our first study, we reported on the stripping behavior of bare carbon electrode in micro-flow sensor for trace measurements of Pb(II) and Cd(II).

3.1 Long-term stability and reproducibility of carbon electrode

The long-term stability of the carbon electrode is important parameter for automatic monitoring. Hence, the long-term stability of the carbon electrode was tested by monitoring of the current signal of Cd(II) and Pb(II) for a period of time. The experimental conditions for the differential pulse anodic stripping voltammetry were investigated with 50 ppb Cd(II) and

Pb(II) in 1.0 M HCl. A pre-concentration potential of -1.20 V was applied to the working electrode under flow conditions for 180 s. After the accumulation, an equilibration period of 10 s at the stopped-flow system and an anodic stripping voltammetric scan (initial potential -1.20 V; final potential 0.60 V; step potential 5 mV; conditioning time 5 s) were applied to the working electrode and the voltammogram was recorded. The experimental sequence for on-line stripping voltammetry was based on the procedure in Table 1. The electrode was found to be stable, even after 10 voltammetric scans. The inter- and intra-day reproducibility of the electrode were determined by 10 replicate measurements during three operating days. The corresponding

voltammograms were analyzed and data were presented in Table 2 and Table 3 in term of average peak heights. The results in Table 2 and 3 showed a good reproducibility of the carbon electrode in micro-flow system with relative standard deviation less than 10 %. From the data in Table 3, average stripping peak current in each measurement within a day (n = 10 per day) was obtained in a range of 0.62 to 0.80 μA for Cd(II) and in a range of 0.61 to 0.65 μA for Pb(II). The analysis time was 11.2 min, including aspiration and dispensation of the solutions to the micro-flow sensor by SIA system and stripping voltammetric procedure. Relative standard deviation of three micro-flow sensors was found to be in a range of 9.1 to 10.5 % for Cd(II) and 1.5 to 7.4 % for Pb(II), observed by inter-day analysis. The carbon electrode in micro-flow sensor is quite stable; one electrode can be used for 4 days. Thus the carbon electrode can be used as an effective sensor with good reproducibility, long stability and short analysis time for metal ion determination.

Table 2 Stripping currents and reproducibility for 50 ppb Cd(II) and Pb (II) in 1.0 M HCl measured in micro-flow system (intra-day analysis: n = 10)

N	Average current (μA)					
	Cd(II)			Pb(II)		
	Day ¹			Day ¹		
	(A)	(B)	(C)	(A)	(B)	(C)
1	0.75	0.72	0.70	0.66	0.65	0.61
2	0.64	0.89	0.91	0.62	0.65	0.61
3	0.57	0.71	0.68	0.65	0.65	0.60
4	0.64	0.88	0.71	0.64	0.59	0.68
5	0.65	0.89	0.79	0.70	0.59	0.69
6	0.56	0.74	0.75	0.64	0.69	0.61
7	0.56	0.75	0.70	0.64	0.60	0.61
8	0.62	0.76	0.68	0.60	0.65	0.59
9	0.60	0.83	0.68	0.69	0.63	0.58
10	0.59	0.82	0.78	0.67	0.67	0.55
Average	0.62	0.80	0.74	0.65	0.64	0.61
SD	0.06	0.07	0.07	0.03	0.03	0.04
%RSD	9.4	9.1	9.9	4.7	5.5	6.8

¹ (A) October 24th, 2008; (B) October 25th, 2008; (C) October 29th, 2008.

3.2 Differential pulse anodic stripping voltammetry (DPASV)

Anodic stripping voltammetric method is based on electrochemical reduction of metal ions at a working electrode to deposit the metals on the electrode surface and subsequent anodic stripping by scanning the potential to anodic direction to allow electrooxidation of the deposited metals at a characteristic potential of each metal, as recorded as a voltammogram in this step. Optimum conditions for deposition and stripping steps of DPASV of Cd(II) and Pb(II) on the carbon electrode in micro-flow sensor coupled with on-line Auto-Pret system were investigated.

3.2.1 Effect of deposition potential

The influence of the deposition potential applied to the carbon electrode in micro-flow sensor on the peak currents was studied from -0.90 V to -1.40 V and the results are shown in Figure 2. It was found that the more negative potential used, the higher sensitivity was obtained up to -1.20 V, after that the sensitivity was slightly decrease. Therefore, the deposition potential of -1.20 V was selected.

Table 3 Comparison of the stripping currents and the reproducibility between days for 50 ppb of Cd(II) and Pb(II) in 1.0 M HCl using micro-flow system

μ -flow number	Date measured	Cd(II)		Pb(II)	
		Average current (μA)	%RSD	Average current (μA)	%RSD
1	8-Oct	0.70 \pm 0.07	10.4	0.55 \pm 0.03	6.1
	10-Oct	0.70 \pm 0.07	10.2	0.55 \pm 0.04	7.4
	14-Oct	0.72 \pm 0.07	9.6	0.48 \pm 0.32	6.5
2	24-Oct	0.62 \pm 0.06	9.4	0.65 \pm 0.03	4.7
	25-Oct	0.80 \pm 0.07	9.1	0.64 \pm 0.03	5.5
	29-Oct	0.74 \pm 0.07	9.9	0.61 \pm 0.04	6.8
3	30-Oct	0.77 \pm 0.08	10.1	0.56 \pm 0.03	4.8
	31-Oct	0.71 \pm 0.07	10.5	0.54 \pm 0.01	1.5
	3-Nov	0.78 \pm 0.08	10.1	0.55 \pm 0.03	4.9

3.2.2 Effect of pulse time and pulse potential

Other parameters which influence differential pulse anodic stripping operation are pulse time and pulse potential. The effect of the pulse time upon the stripping responses for 50 ppb of both Cd(II) and Pb(II) was investigated in the range of 0.01 to 0.25 s. As shown in Figure 3A, the signals for both analytes decreased with increasing the pulse time. Therefore, the optimal pulse time of 0.01 s was chosen. The influence of pulse potential on the stripping peak currents was also examined in the range of 5 to 100 mV, the results are plotted in Figure 3B. The optimized pulse potential of 50 mV was selected for the simultaneous determination of Cd(II) and Pb(II).

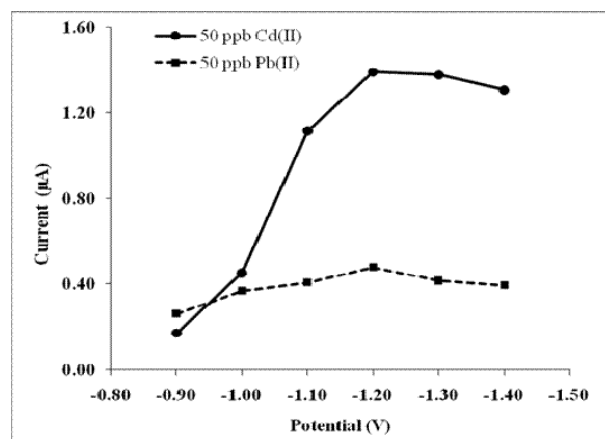


Fig. 2 Effect of the deposition potential on the peak heights for a solution containing 50 ppb each of Cd(II) and Pb(II) on carbon electrode in micro-flow sensor. Conditions: deposition time, 180 s; step potential, 0.005 V; conditioning potential, -1.00 V; scan rate, 0.005 V s⁻¹; quiet time, 10 s.

3.3 Square-wave anodic stripping voltammetry (SWASV)

Among the stripping waveforms, the square-wave modulation combines high sensitivity with high speed. The square-wave form was found to be preferable to both the differential pulse and the linear scan stripping waveforms for anodic stripping voltammetric method. One additional advantages of the square-wave form is its insensitivity to dissolved oxygen which allowed the analysis to be carried out in the presence of oxygen and

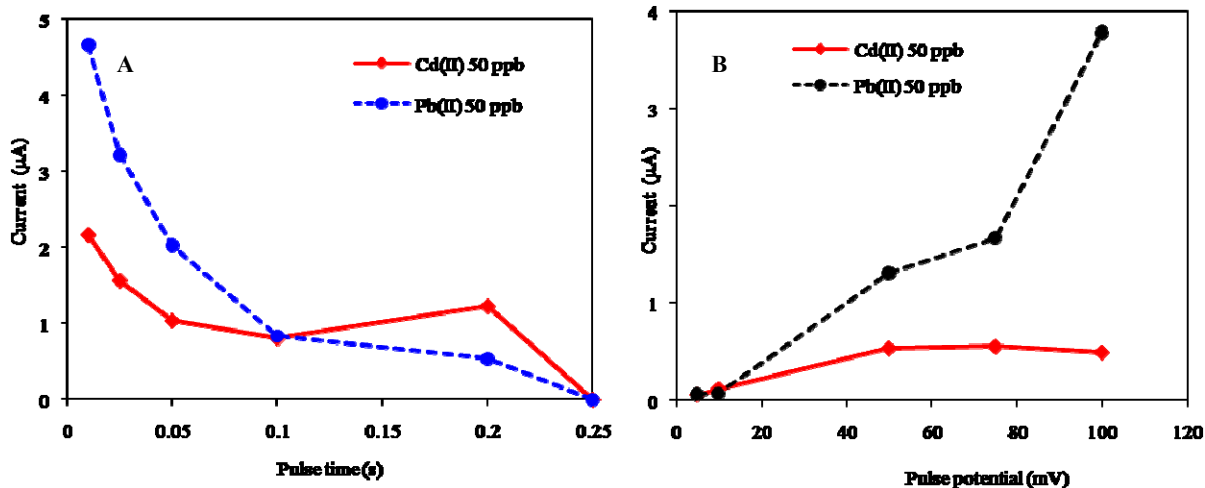


Fig. 3 Effect of the pulse time (A) and pulse potential (B) for 50 ppb Cd(II) and Pb(II) solution by differential pulse anodic stripping voltammetry (DPASV). Conditions: deposition potential, -1.20 V; deposition time, 180 s; step potential, 0.005 V; conditioning potential, -1.00 V; scan rate, 0.005 V s⁻¹; quiet time, 10 s.

avoided the time-consuming deoxygenation step. Differential pulse and square-wave anodic stripping voltammograms of 50 ppb Cd(II) and Pb(II) on the carbon electrode in micro-flow sensor are compared in Figure 4. The stripping currents of Cd(II) and Pb(II), measured after accumulation for 180 s at a potential of -1.20 V on different sections ($n = 3$) of the carbon electrode in the same micro-flow sensor and same analysis day were found to be $2.43 \pm 0.14 \mu\text{A}$ (RSD = 5.9 %) and $8.98 \pm 0.04 \mu\text{A}$ (RSD = 0.5 %) for Cd(II) determination by DPASV and SWASV, respectively; and $3.47 \pm 0.33 \mu\text{A}$ (RSD = 9.6 %) and $10.29 \pm 0.31 \mu\text{A}$ (RSD = 3.0 %) for Pb(II) determination by DPASV and SWASV, respectively.

Optimization of experimental conditions for SWASV of Cd(II) and Pb(II) on the carbon electrode in micro-flow sensor coupled

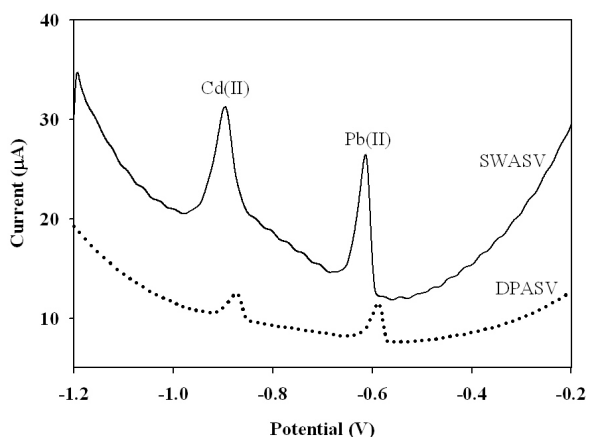


Fig. 4 Comparison of differential-pulse anodic stripping voltammogram (DPASV) and square-wave anodic stripping voltammogram (SWASV) of 50 ppb of Cd(II) and Pb(II) using micro-flow sensor. DPASV conditions: deposition potential, -1.20 V, 180 s of the deposition time, 0.005 V step potential, -1.00 V conditioning potential, pulse time 0.01 s, pulse potential 0.05 V, 0.005 V/s of scan rate, conditioning time at 5 s and quiet time 10 s, scan the potential from -1.20 to 0 V. SWASV conditions: deposition potential -1.20 V, 180 s of the deposition time, 0.005 V step increment, -1.00 V conditioning potential, pulse height 0.05 V, conditioning time at 5 s and quiet time 10 s, scan the potential from -1.20 to 0 V.

with on-line Auto-Pret system were performed by using the step sequence for on-line determination in Table 1. In this technique, the analysis time was decreased from 11.2 min (section 3.1) to 3.65 min because the advantage of the fast scans measuring. The effect of the deposition potential was studied in a range of -0.90 to -1.50 V with a solution containing 50 ppb of Cd(II) and Pb(II) in 1.0 M HCl. The peak height increased linearly with the deposition potential. This dependence could be used for increasing the sensitivity in SWASV. The deposition potential at -1.50 V gave a high peak current but the peak shape was easily destroyed due to the more negative potential in acid media could destroy the metal alloys deposited and the hydrogen evolution could occur [6]. From the result, the deposition potential at -1.40 V was selected as the optimum potential.

The effect of the square-wave frequency was studied in a range of 10 – 75 Hz and the effect of the step increment was investigated between 2.5 and 10 mV. The peak potentials shifted to the anodic direction with increasing frequency or step increment. These observations were agreed with the results obtained by G. Kefala, et al [9]. The peak heights for Cd(II) and Pb(II) increased at higher step increments, whereas the Cd(II) and Pb(II) peak currents increased until the frequency reach 50 Hz. The effect of the square-wave pulse height was also studied in a range from 10 to 75 mV. The peak potentials were shifted to the cathodic direction and the peak heights increased upon increasing of the pulse height. However, the background current slightly increased at higher pulse heights. Hence, the optimum square-wave conditions were fixed at the square-wave frequency 50 Hz, the step increment 75 mV and pulse height 5 mV. The optimized experimental conditions for SWASV of Cd(II) and Pb(II) on the carbon electrode in micro-flow sensor were summarized in Table 4.

3.4 Analytical performance of the method

At the optimum experimental conditions, the electroanalytical performance of on-line DPASV and SWASV of Cd(II) and Pb(II) on the carbon electrode in micro-flow sensor were examined. The linear relationship between the current responses and the concentration were obtained in the concentration range of 5.0 – 75.0 ppb for Cd(II) and 2.5 – 75.0 ppb for Pb(II). Figure 5A and 5B show the calibration plot of Cd(II) and Pb(II) obtained from DPASV and SWASV. The limit of detection (LOD, S/N = 3) were 2.37 ppb and 0.15 ppb for the determination of Cd(II) and

Table 4 Optimized experimental parameters for on-line DPASV and SWASV for Cd(II) and Pb(II) on the carbon electrode in micro-flow sensor coupled with Auto-Pret system

Parameters	DPASV	SWASV
Deposition potential (V)	-1.20	-1.40
Pulse potential (V)	0.05	-
Pulse time (s)	0.01	-
Square-wave increment (V)	-	0.0075
Pulse height (V)	-	0.05
Square-wave frequency (Hz)	-	50

Pb(II) by DPASV and 0.02 ppb and 0.01 ppb for the determination of Cd(II) and Pb(II) by SWASV. The relative standard deviations were 7.6 % and 4.0 % for the determination of 50 ppb Cd(II) and Pb(II) by DPASV and 5.1 % and 3.2 % for the determination of 50 ppb Cd(II) and Pb(II) by SWASV.

Analytical characteristics of both methods are summarized in Table 5. The results obtained prove that on-line SWASV on the carbon electrode in micro-flow sensor possesses the best analytical characteristics on three key parameters: high sensitivity, good reproducibility and short analysis time. Consequently, this proposed method is feasible for the determination of metals in real samples.

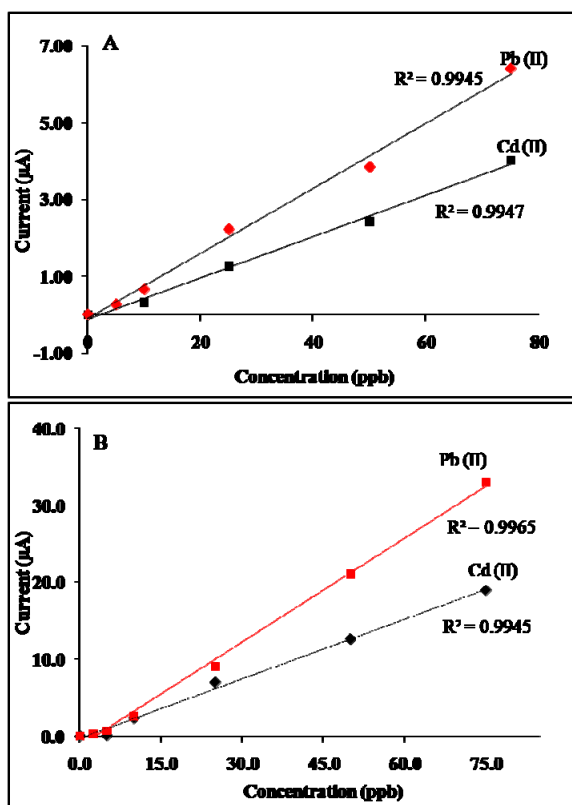


Fig. 5 The calibration plot of 50 ppb Cd(II) and Pb(II) in 1.0 M HCl at the linear concentration range for DPASV (A) and SWASV (B). DPASV conditions: deposition potential, -1.20 V; deposition time, 180 s; step potential, 0.005 V; conditioning potential, -1.00 V; pulse time, 0.01 s; scan rate, 0.005 V s⁻¹; quiet time, 10 s. SWASV conditions: deposition potential, -1.40 V; deposition time, 180 s; square wave increment, 0.0075 s; conditioning potential, -1.00 V; pulse height, 0.05 V; square wave frequency, 50 Hz; scan rate, 0.005 V s⁻¹; quiet time, 10 s.

Table 5 Analytical performance of on-line DPASV and SWASV method for Cd(II) and Pb(II) on the carbon electrode in micro-flow sensor coupled with Auto-Pret system at the optimal experimental conditions

Metal ion	Method	Linear range (ppb)	R ²	Average current ^a (µA)	LOD (ppb)	RSD ^a (%)
Cd(II)	DPASV	10.0 – 75.0	0.9947	2.50 ± 0.19 ^b	2.37	7.6
	SWASV	5.0 – 75.0	0.9945	13.20 ± 0.67	0.02	5.1
Pb(II)	DPASV	5.0 – 75.0	0.9945	3.41 ± 0.14	0.15	4.0
	SWASV	2.5 – 75.0	0.9965	13.09 ± 0.51	0.01	3.2

^a At the concentration 50 ppb (n = 3)

^b Standard deviation

4. Conclusions

The characteristics of carbon electrode in micro-flow sensor were studied by on-line determination of Cd(II) and Pb(II) base on electrochemical stripping method. The sensor showed a linear response in the concentration range of 5.0 – 75.0 ppb for Cd(II) and 2.5 – 75.0 ppb for Pb(II). The carbon electrode showed excellent response and the LOD values obtained for the determination of model metals were found to be in very low ppb levels. This electrode provided good reproducibility and was stable for at least 4 days (160 samples). In the future work, we plan to report the efficiency of the preconcentration membrane in the micro-flow sensor for Cd(II) and Pb(II) determination in real samples.

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