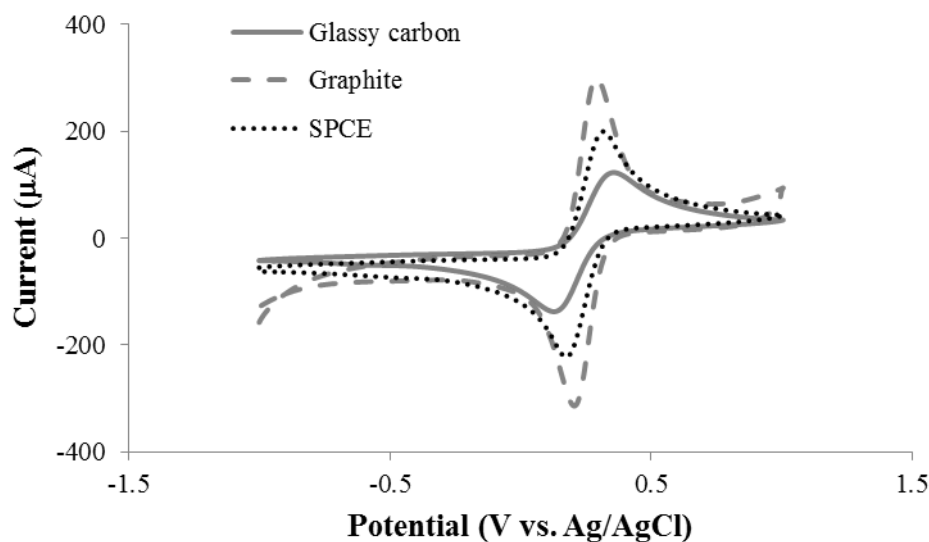


## CHAPTER 3

### Results and Discussion

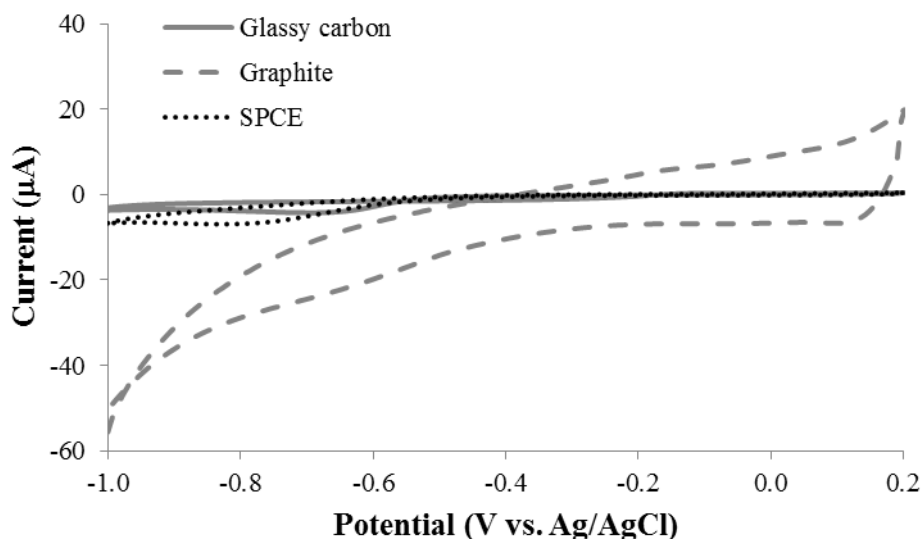
#### 3.1 Sensitivity of different carbon electrodes

The capacitance and sensitivity of different carbon materials including glassy carbon, graphite and SPCE (the pictures of electrodes are shown in appendix A) were compared by the measurements of cyclic voltammetry and anodic stripping voltammetry. Figure 3.1 shows the cyclic voltammograms obtained by using glassy carbon, graphite and SPCE in 10 mM potassium ferricyanide solution (containing 0.1 M KCl electrolyte solution). All three electrodes can detect redox reaction of ferricyanide, graphite electrode exhibited the highest signal because it may has highest active surface area.



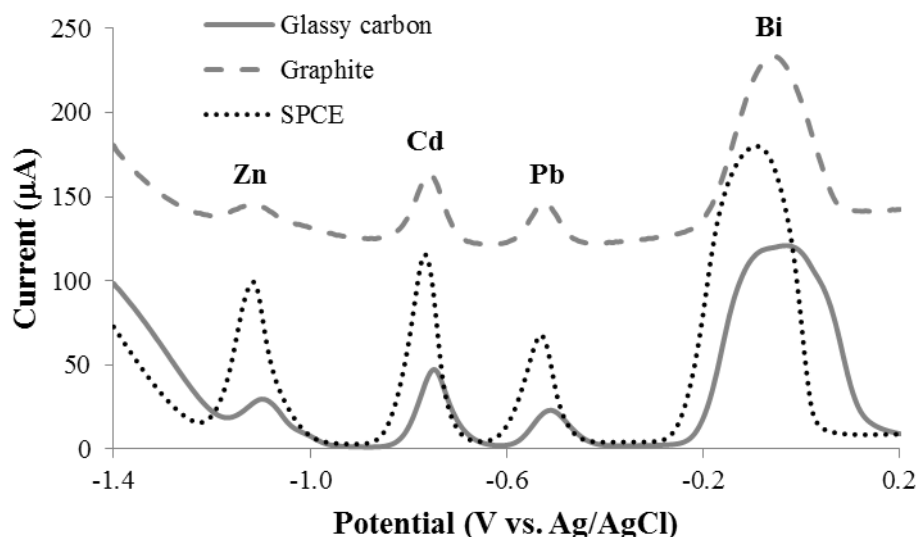
**Figure 3.1** The cyclic votammograms of a bare glassy carbon, graphite and SPCE electrode in 0.1 M KCl solution containing 10 mM  $K_3Fe(CN)_6/K_4Fe(CN)_6$  at a scan rate  $100 \text{ mV s}^{-1}$  ( $\varnothing$  3 mm for each electrode)

As can be seen from CV studied in 0.1 M acetate buffer solution (pH 4.5), the graphite electrode gave the highest capacitive current because it has the largest effective surface area. Glassy carbon and SPCE has wider potential window and lower background current as shown in Figure 3.2.



**Figure 3.2** The cyclic voltammograms of a bare glassy carbon, graphite, and SPCE electrode in 0.1 M acetate buffer solution (pH 4.5) at scan rate  $100 \text{ mV s}^{-1}$  ( $\varnothing 3 \text{ mm}$  for each electrode)

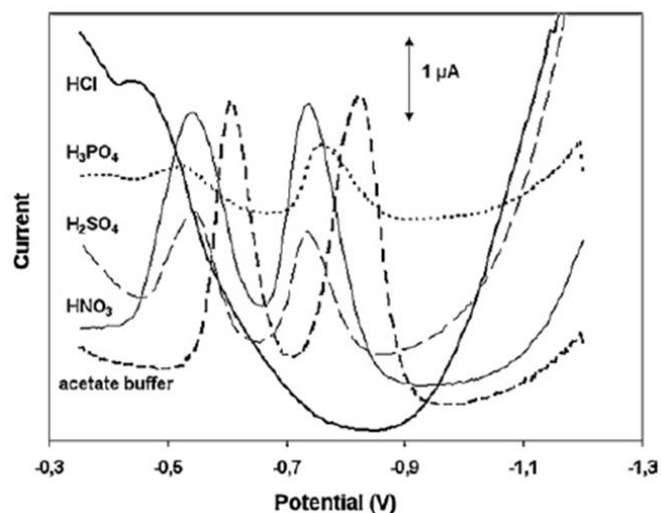
When the bismuth film was plated on the three electrodes, the voltammograms of the bismuth plated SPCE electrode exhibited the sharpest and the highest peak current. And the sensitivity of the Bi-SPCE electrode was higher than that of the glassy carbon and graphite electrode. According to Figure 3.3, the SPCE is the suitable working electrode for the determination of cadmium, lead and zinc. The effect of concentration and pH of acetate buffer solution, concentration of bismuth(III), deposition time, deposition potential and rotation speed of stirrer will be further investigated.



**Figure 3.3** The anodic stripping voltammograms of  $30 \mu\text{g L}^{-1}$  for cadmium, lead and zinc at *in situ* plated bismuth film obtaining from  $1.0 \text{ mg L}^{-1}$  of bismuth(III) concentration plating solution on glassy carbon, graphite and SPCE electrodes. Supporting electrolyte: 0.1 M acetate buffer solution (pH 4.5); deposition potential: -1.2 V; deposition time: 300 s; frequency: 50 Hz; voltage step: 5 mV ( $\varnothing$  3 mm for each electrode)

### 3.2 Optimization of ASV system using Bi-SPCE as a working electrode

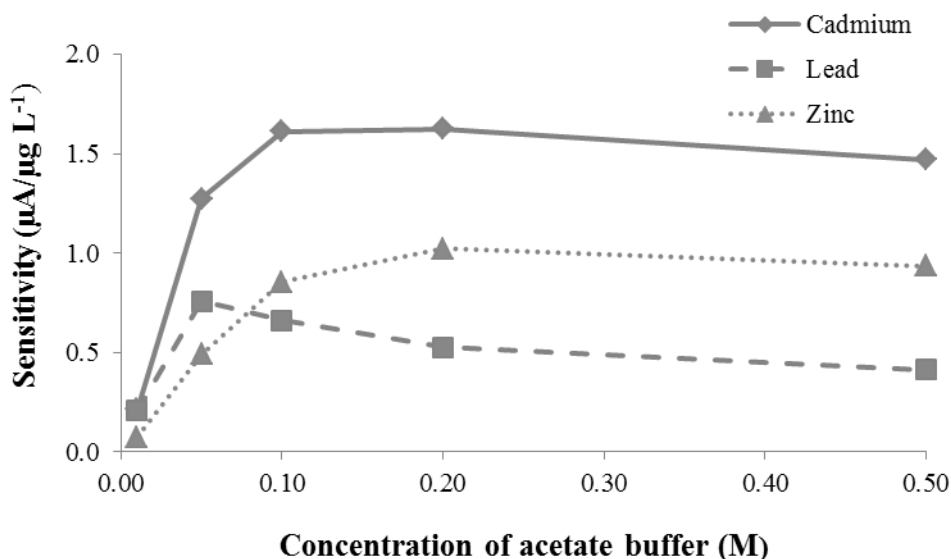
Since the heavy metal ions have different electrochemical behaviors in different electrolytes. Lezi *et al.* studied the effect of several electrolytes such as 0.05 M of hydrochloric acid, phosphoric acid, sulphuric acid, nitric acid and 0.1 M acetate buffer (pH 4.5). They found that the acetate buffer exhibited the best background and highest response for the cadmium and lead peaks because higher pH suppressed the hydrogen evolution which was more pronounced in the acidic solutions as depicted in Figure 3.4. In the case of hydrochloric acid medium no peak was observed, this was attributed to the electrode inactivation by the formation of irreversibly reducible bismuth oxychloride ( $\text{BiOCl}$ ) [Lezi *et al.*, 2012]. Thus in this work, the effect of concentration and pH of acetate buffer solution will be studied.



**Figure 3.4** Comparative square wave voltammograms at screen-printed electrode modified with 6% (w/w) bismuth citrate in 0.05 M of hydrochloric acid, phosphoric acid, sulphuric acid, nitric acid and 0.1 M acetate buffer (pH 4.5) containing  $40 \mu\text{g L}^{-1}$  for cadmium and  $20 \mu\text{g L}^{-1}$  for lead, deposition time 120 s, deposition potential -1.4 V [Lezi *et al.*, 2012]

### 3.2.1 Effect of concentration of acetate buffer solution

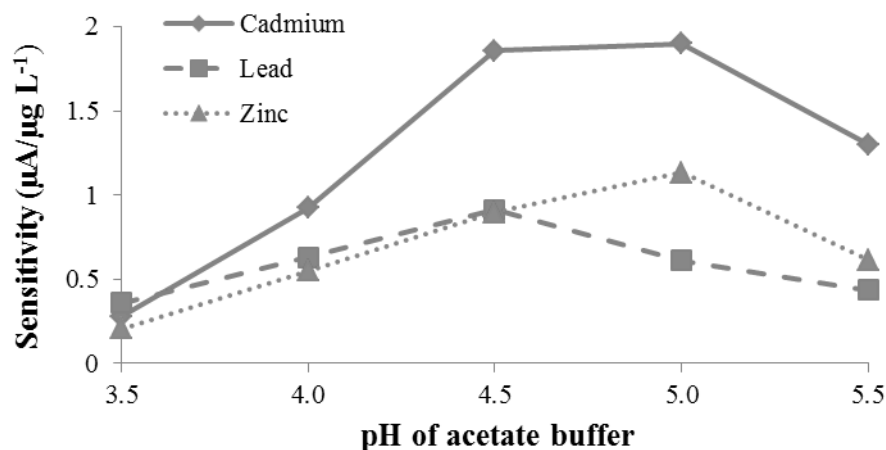
The supporting electrolyte behavior is probably associated with the mechanism of the formation of the metallic bismuth, the reaction of the target metals ions to form an alloy with bismuth. The optimization of concentration of acetate buffer solution for the simultaneous determination of cadmium, lead and zinc by SWASV on the *in situ* Bi-SPCE was carried out by increasing the metal concentration from  $5$  to  $30 \mu\text{g L}^{-1}$  for cadmium and lead, and  $10$  to  $60 \mu\text{g L}^{-1}$  for zinc, and applying a deposition potential of  $-1.2$  V and deposition time of  $300$  s in acetate buffer solution (pH 4.5) the slope of calibration graphs when varying concentration of acetate buffer solution in the range of  $0.01$  to  $0.50$  M was considered as shown in Figure 3.5. A better performance was observed at concentration of acetate buffer solution at  $0.1$  M. At lower concentration, ionic strength of buffer solution is not enough for good electrical conductivity of the solution and electron transfer, and at higher concentration of buffer solution, the peak current was decreased due to lower mass transfer in the higher ionic strength solution, resulting in lower sensitivity of the analysis.



**Figure 3.5** The effect of concentration of acetate buffer solution on the sensitivity (slope) of cadmium, lead and zinc determination on Bi-SPCE at of bismuth plating solution. At different concentration of acetate buffer solution (0.01, 0.05, 0.10, 0.20 and 0.50 M) and other conditions are the same as in Figure 3.3

### 3.2.2 Effect of pH of acetate buffer solution

The effect of pH on the stripping peak current was studied in 0.1 M acetate buffer solution, with pH values ranging from 3.5 to 5.5 as shown in Figure 3.6. The best signals for cadmium and lead were observed at mildly acidic pH 4.5. In the case of zinc, the high signal was observed at pH 5.0. To obtain good sensitivity for the target metal ions, pH 4.5 was selected as the optimal pH value for experiment. At lower pH, the decrease of the peak current because the SPCE surface may be occur hydrogen gas ( $H_2$ ) from reduction of hydrogen ions ( $H^+$ ) in electrolyte solution that could damage the bismuth film. At higher pH the peak current decrease is possibly due to formation of metal hydroxide complexes because the solubility product constants ( $K_{sp}$ ) of cadmium hydroxide ( $7.2 \times 10^{-15}$ ), lead hydroxide ( $1.43 \times 10^{-20}$ ) and zinc hydroxide ( $3 \times 10^{-17}$ ) are very lower than the concentration of hydroxide ions.

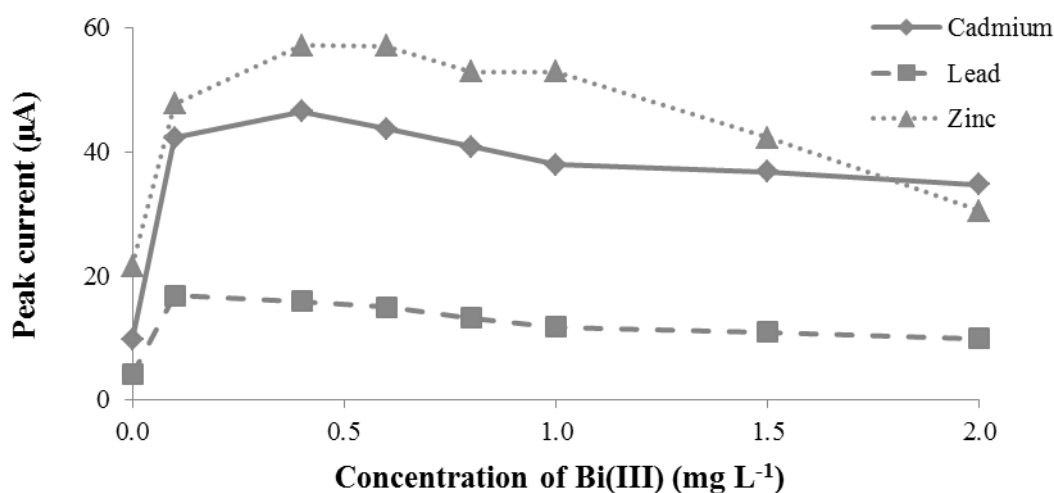


**Figure 3.6** The effect of pH of acetate buffer solution on the sensitivity (slope) of cadmium, lead and zinc determination. At different pH of acetate buffer solution (3.5, 4.0, 4.5, 5.0 and 5.5) and other conditions are the same as in Figure 3.3

### 3.2.3 Effect of bismuth concentration

The concentration of bismuth controlled the thickness of the bismuth film, in turn affecting the electrochemical response of Bi-SPCE composite electrode. The influence of the bismuth ion concentration on the stripping signal of 30  $\mu\text{g L}^{-1}$  cadmium and lead and 60  $\mu\text{g L}^{-1}$  zinc was investigated. In Figure 3.7, the peak heights for metal ions increased with increasing bismuth concentration from 0.1 to 0.4  $\text{mg L}^{-1}$  and decreased above 0.6  $\text{mg L}^{-1}$  because the saturation of bismuth film on the SPCE electrode. Accordingly, the optimum concentration of bismuth was chosen at 0.4  $\text{mg L}^{-1}$ .

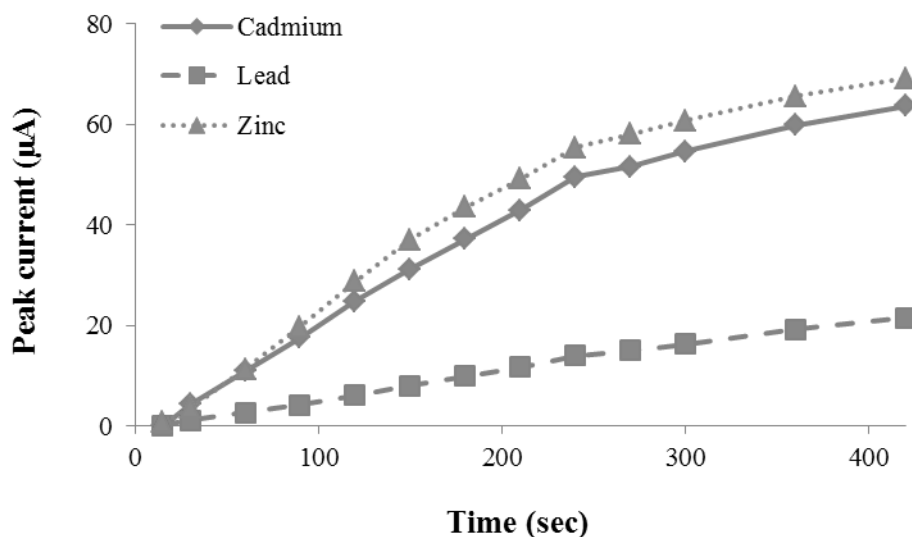
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**Figure 3.7** The effect of bismuth(III) concentration on the stripping peak current of 30  $\mu\text{g L}^{-1}$  cadmium and lead, and 60  $\mu\text{g L}^{-1}$  zinc on Bi-SPCE at different bismuth(III) concentration (0.0, 0.1, 0.4, 0.6, 0.8, 1.0, 1.5 and 2.0  $\text{mg L}^{-1}$ ) plating solution and other conditions are the same as in Figure 3.3

### 3.2.4 Effect of deposition time

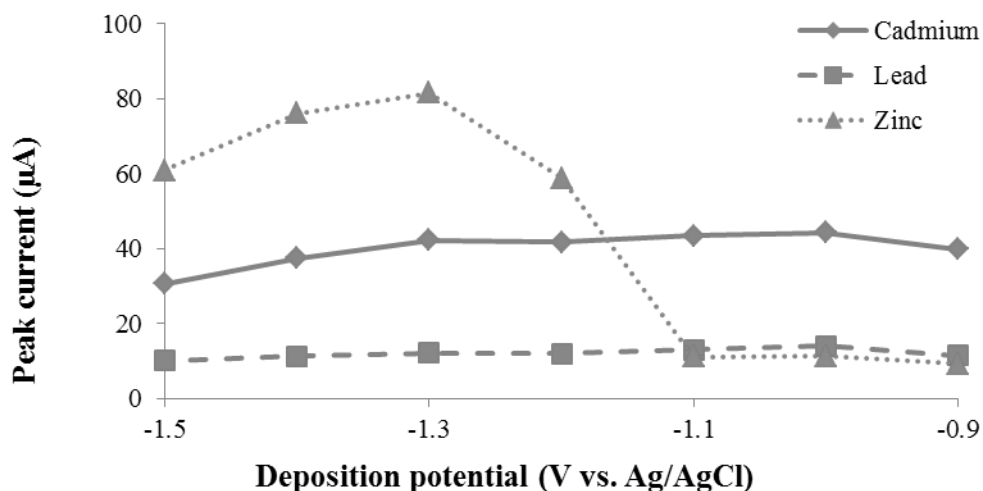
In Figure 3.8, the influence of the deposition time was studied over time intervals from 15 to 420 s. The peak current continuously increased with increasing of time to deposit. However, the slope of the graph tended to diminish for values up to 240 s due to the saturation effect of the bismuth film. Thus, 240 s was chosen to be the optimal preconcentration/deposition time.



**Figure 3.8** The effect of deposition time on the stripping peak current of  $30 \mu\text{g L}^{-1}$  cadmium and lead, and  $60 \mu\text{g L}^{-1}$  zinc on Bi-SPCE at  $0.4 \text{ mg L}^{-1}$  bismuth(III) concentration plating solution. At different depositions time (15, 30, 60, 90, 120, 180, 210, 270, 300, 360 and 420 s) and other conditions are the same as in Figure 3.3

### 3.2.5 Effect of deposition potential

The effect of the deposition potential on peak current of heavy metal ions was investigated in the potential range from  $-0.9$  to  $-1.5$  V and the stripping currents of the metal ions was considered. In Figure 3.9, as the deposition potential become more negative, the peak current of cadmium and lead are quite stable so no significant increase in the peak current, while the maximum peak current of zinc was observed at potential  $-1.3$  V, and the peak current of zinc decreased above  $-1.4$  V due to hydrogen evolution at this negative potential. Thus, a deposition potential of  $-1.3$  V was considered to be optimum to achieve good sensitivity for all three heavy metal ions.

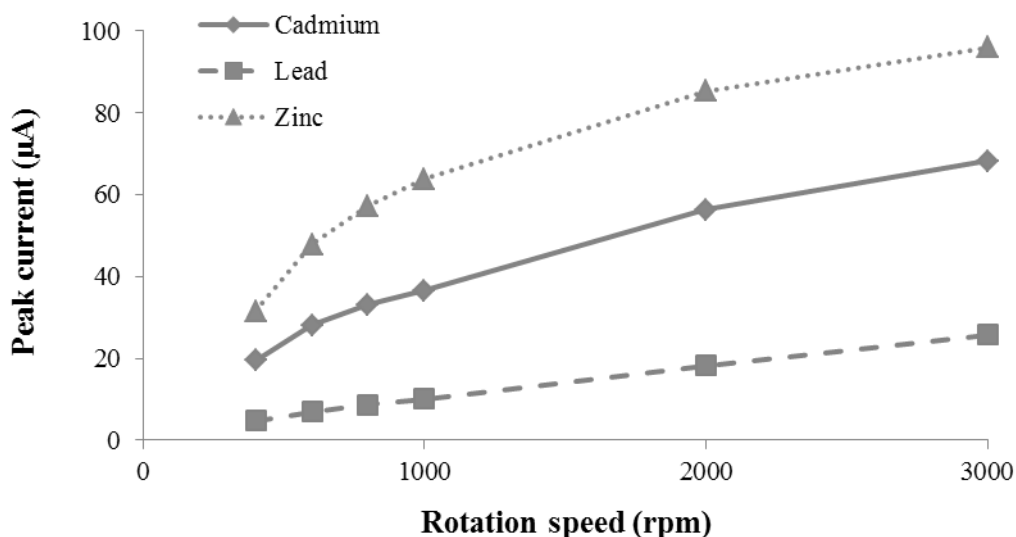


**Figure 3.9** The effect of deposition potential on the stripping peak current of  $30 \mu\text{g L}^{-1}$  cadmium and lead, and  $60 \mu\text{g L}^{-1}$  zinc on Bi-SPCE at  $0.4 \text{ mg L}^{-1}$  of bismuth(III) concentration plating solution and deposition time 240 s. At different depositions potentials (-0.9, -1.0, -1.2, -1.3, -1.4 and -1.5 V) and other conditions are the same as in Figure 3.3

### 3.2.6 Effect of rotation speed of stirrer

The mass transfer behavior during preconcentration step was investigated by varying the rotation speed in the range of 400 to 3000 rpm as shown in Figure 3.10. The stripping peak currents for cadmium, lead and zinc continuously increased with the increase of rotation speed. The 3000 rpm is a maximum rotation speed of the equipment but very high rotation speeds increased the risk of the bismuth film being mechanically damaged, thus the preconcentration was performed at 2000 rpm.

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**Figure 3.10** The effect of rotation speed during deposition step on the stripping peak current of  $30 \mu\text{g L}^{-1}$  cadmium and lead, and  $60 \mu\text{g L}^{-1}$  zinc on Bi-SPCE at  $0.4 \text{ mg L}^{-1}$  of bismuth(III) concentration plating solution, deposition time 240 s and deposition potential -1.3 V. At different speeds (400, 600, 800, 1000, 2000 and 3000 rpm) and other conditions are the same as in Figure 3.3

### 3.2.7 The optimum operational conditions

The parameters which affected analytical performance and the optimum condition for the simultaneous determination of cadmium, lead and zinc using ASV with Bi-SPCE are summarized in the Table 3.1.

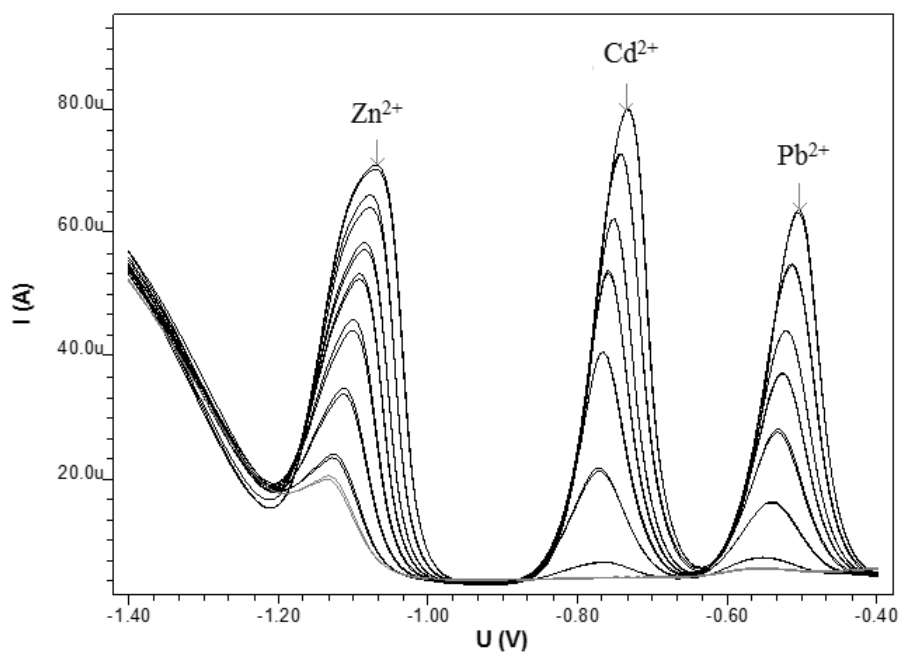
**Table 3.1** The optimum operating parameters for the simultaneous determination of cadmium, lead and zinc by ASV

Parameter	Description
Concentration of acetate buffer solution	0.10 M
pH of acetate buffer solution	4.5
Concentration of bismuth(III) plating solution	$0.4 \text{ mg L}^{-1}$
Deposition time	240 s
Deposition potential	-1.3 V
Rotation speed	2000 rpm

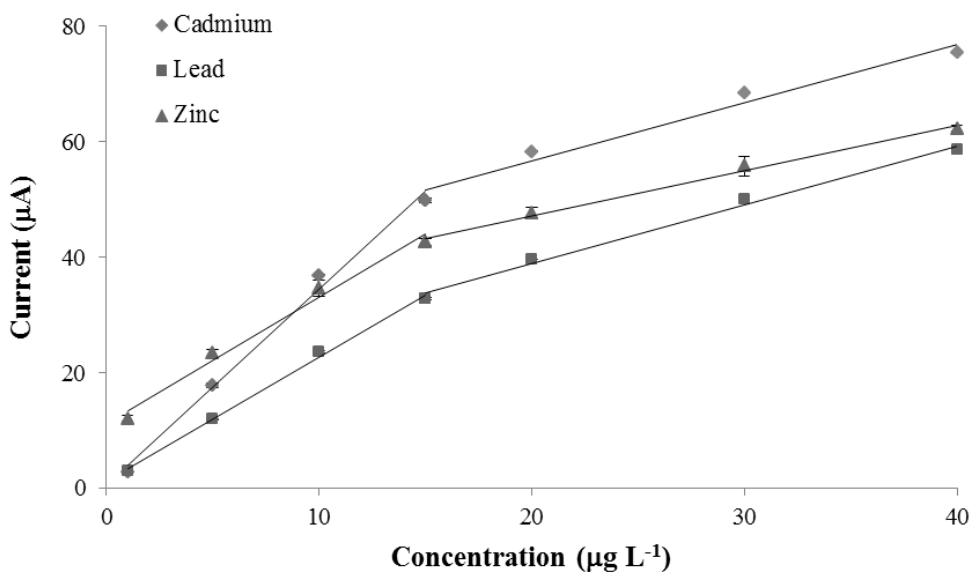
### 3.3 Analytical characteristics

#### 3.3.1 Calibration curve

Under the optimum condition, the analytical performance of the Bi-SPCE as a working electrode was investigated by simultaneous analysis of cadmium, lead and zinc concentration from 1 to 40  $\mu\text{g L}^{-1}$  in 0.1 M acetate buffer solution (pH 4.5) containing 0.4  $\text{mg L}^{-1}$  of bismuth(III) concentration plating solution. The square wave anodic stripping voltammetric response for different concentrations of cadmium, lead and zinc ions is illustrated in Figure 3.11. The calibration graphs of metal ions were constructed by plotting peak current ( $\mu\text{A}$ ) versus metal ions concentration ( $\mu\text{g L}^{-1}$ ) as shown in Figure 3.12.



**Figure 3.11** The stripping voltammograms for various concentrations (1, 3, 5, 10, 15, 20, 30 and 40  $\mu\text{g L}^{-1}$ ) of cadmium, lead and zinc ions on the Bi-SPCE electrode and other conditions are same as in Table 3.1 (page 32)



**Figure 3.12** The calibration graphs for the simultaneous analysis of cadmium, lead and zinc on the Bi-SPCE electrode, error bar:  $n=2$  and other conditions are the same as in Table 3.1 (page 32)

The calibration graphs for cadmium, lead and zinc had two linear ranges which had different slopes at low concentration in the range of  $1.0$  to  $15.0 \mu\text{g L}^{-1}$  and at high concentration in the range of  $15.0$  to  $40.0 \mu\text{g L}^{-1}$ . The linear regression equation and correlation coefficients of calibration of these metals are summarized in Table 3.2. As expected, the limit of active site on surface of the electrode lead to the decrease in sensitivity, at high concentration of metal ions the deposition of target ions was occurred with more thickness than at low concentration. In the stripping step, the oxidation reaction can occur only on the surface of the electrode. The underneath metals cannot be oxidized until the upper layer already oxidized and dissolved into the solution so the current is limited and resulting in lower slope at high concentration of the metals. In this work, we are interested to determine of three metals at trace concentration level, therefore, a linear range of  $1.0$  to  $15.0 \mu\text{g L}^{-1}$  was used in the next experiment.

**Table 3.2** Calibration data for the simultaneous analysis of cadmium, lead and zinc on the Bi-SPCE as a working electrode

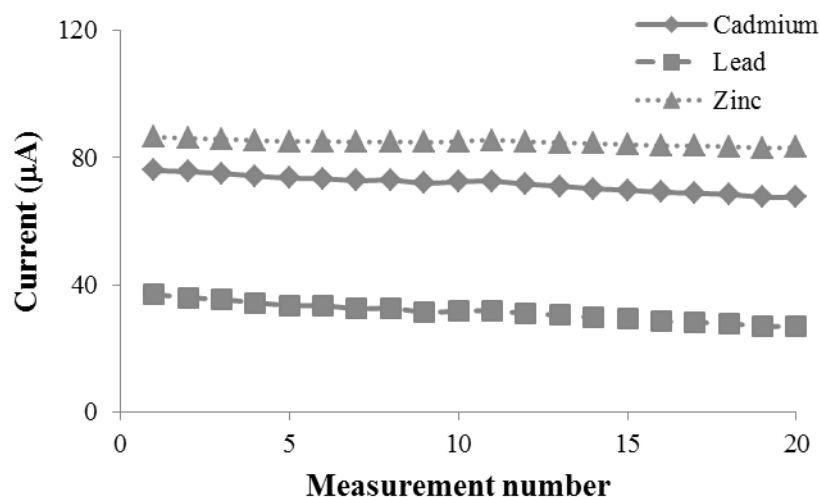
Metals	Regression	R <sup>2</sup>	Linear range (µg L <sup>-1</sup> )
<b>Cadmium</b>	$y = 3.3904x + 0.5672$	0.9923	1.0 - 15.0
	$y = 1.0023x + 36.668$	0.9719	15.0 - 40.0
<b>Lead</b>	$y = 2.1438x + 1.2103$	0.9970	1.0 - 15.0
	$y = 1.0212x + 18.4010$	0.9923	15.0 - 40.0
<b>Zinc</b>	$y = 2.1761x + 11.2800$	0.9861	1.0 - 15.0
	$y = 0.7818x + 31.5370$	0.9923	15.0 - 40.0

### 3.3.2 Limits of detection

The limits of detection (LODs) of metal ions were 0.06 µg L<sup>-1</sup> for cadmium and lead and 0.17 µg L<sup>-1</sup> for zinc. The results and calculation procedure are given in appendix B.

### 3.3.3 Precision

A series of repetitive anodic stripping voltammetric response measurements of 30 µg L<sup>-1</sup> cadmium and lead, and 60 µg L<sup>-1</sup> zinc in 0.1 M acetate buffer solution (pH 4.5) were performed to further evaluate the stability of the Bi-SPCE electrode. Repeatability was evaluated from a relative standard deviation (RSD) for 20 replicates determination on the same electrode and found to be 3.6 % for cadmium, 9.5 % for lead, and 1.1 % for zinc as shown in Figure 1.13. The Bi-SPCE electrode has good precision for repetitive ASV measurements. The reproducibility was studied by measuring the signal of 30 µg L<sup>-1</sup> cadmium and lead, and 60 µg L<sup>-1</sup> zinc in 0.1 M acetate buffer solution (pH 4.5) on 9 electrodes and the results obtained were 7.7 %RSD for cadmium, 6.7 %RSD for lead, and 8.6 %RSD for zinc as shown in Table 3.3.



**Figure 3.13** Signal stability for 20 repetitive measurements of cadmium and lead ( $30 \mu\text{g L}^{-1}$  each), and zinc ( $60 \mu\text{g L}^{-1}$ ) in  $0.1 \text{ M}$  acetate buffer solution ( $\text{pH } 4.5$ ) on a single Bi-SPCE electrode and other conditions are the same as in Table 3.1 (page 32)

**Table 3.3** The Bi-SPCE reproducibility of signal of cadmium and lead ( $30 \mu\text{g L}^{-1}$  each), and zinc ( $60 \mu\text{g L}^{-1}$ ) in  $0.1 \text{ M}$  acetate buffer solution ( $\text{pH } 4.5$ ) on 9 electrodes and other conditions are the same as in Table 3.1

Bi-SPCE	Current ( $\mu\text{A}$ ) <sup>a</sup>		
	Cadmium	Lead	Zinc
1	82.12	37.91	97.00
2	76.45	31.98	89.60
3	80.87	35.29	89.70
4	66.43	32.34	76.79
5	67.81	35.80	77.56
6	69.75	32.63	75.98
7	76.56	33.16	87.77
8	75.58	30.81	88.52
9	80.31	35.21	91.30
<b>Mean</b>	75.10	33.90	86.02
<b>S.D.</b>	5.82	2.27	7.43
<b>%RSD</b>	7.7	6.7	8.6

<sup>a</sup> Average value of three determinations

### 3.4 Interferences

The interference study was performed by adding various potentially interfering metal cations probably due to competition with the analyte ions and, anions probably due to complexing with the analyte ions. The interfering metal cations including calcium(II), magnesium(II), ferrous(II) and copper(II) and anions including chloride, sulfate and carbonate at 100, 500 and 1000  $\mu\text{g L}^{-1}$  was added into a standard solution containing of 10  $\mu\text{g L}^{-1}$  for cadmium, lead and zinc under the optimum condition. The results are shown in Table 3.4. At 1000  $\mu\text{g L}^{-1}$  of cations and anions, the interference with the determination of target ions was observed. Copper ion is the stronger inference because it can compete with bismuth ion to deposit on the active site of surface electrode resulting from the close reduction potential of copper and bismuth. To solve this problem, previous studied used the ferrocyanide ion to mask the copper ion [Ping *et al.*, 2014, Zhang *et al.*, 2016].

**Table 3.4** The effect of some interference ions for the peak current response of  $10 \mu\text{g L}^{-1}$  for cadmium, lead and zinc and other conditions are the same as in Table 3.1

Interferences	Add ( $\mu\text{g L}^{-1}$ )	%Difference		
		Cadmium	Lead	Zinc
Calcium(II)	100	0.2	-3.1	1.6
	500	-0.3	-6.0	1.5
	1000	-0.9	-1.0	-1.8
Magnesium(II)	100	-2.5	-5.9	-0.7
	500	-3.5	-8.4	-0.6
	1000	-5.1	-9.7	-1.2
Ferrous(II)	100	-0.6	-1.8	0.9
	500	-2.5	-4.8	-0.2
	1000	-3.1	-6.5	-0.3
Copper(II)	100	-6.0	-3.7	-0.7
	500	-75.7	-57.4	-100
	1000	-93.4	-83.5	-100
Chloride	100	-2.2	-5.9	-1.0
	500	-2.0	-6.9	1.2
	1000	-4.3	-12.8	-0.6
Sulfate	100	-1.8	-5.3	-1.0
	500	-2.5	-10.3	-1.6
	1000	-3.9	-14.0	-2.4
Carbonate	100	1.9	2.9	3.9
	500	-3.1	-5.5	0.7
	1000	-4.6	-8.5	-0.8

### 3.5 Application to wastewater samples

The concentrations of cadmium and lead in 3 water samples collected from natural water around Chiang Mai University were determined by the developed ASV method in 3 sections including original water samples, samples spiking with standard solution of  $10 \text{ mg L}^{-1}$  for cadmium, lead and zinc before (fraction 0) and after passing through the resin column. In case of water that passing through the resin column, the constant flow rate of  $1.0 \text{ mL min}^{-1}$  was used and 50 mL of water eluted from the column were kept in each fraction for 5 fractions. Solutions of fractions 2 and 4 were determined for heavy metal concentrations. All of experiments used 120 s of deposition time and other conditions are the same as optimum conditions that summarized in Table 3.1. The concentration of cadmium, lead and zinc are obtained in less than 30 min in one sample. In addition, recoveries were examined by adding of 3 and  $6 \text{ } \mu\text{g L}^{-1}$  cadmium and lead to the sample, and the results were presented in Table 3.5. It was found that the accuracy of the ASV method for determining the concentration of cadmium and lead found the recoveries in the range of 81.2% to 115.3%. In case of zinc recoveries are very high which may be due to the formation of zinc and copper intermetallic compounds and in the natural water have high level of zinc ions. Thus, this work did not focus on the zinc determination of trace heavy metals in water sample. The ASV with Bi-SPCE has been successfully applied in the determination of trace cadmium and lead in water treatment.

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**Table 3.5** Result for determination of trace heavy metal ions in water treatment samples

Sample	Metal found ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>			Add ( $\mu\text{g L}^{-1}$ )	Recovery (%)		
	Cadmium	Lead	Zinc		Cadmium	Lead	Zinc
<b>No. 1</b>	0.64 ± 0.05	2.86 ± 0.17	8.24 ± 0.49	<b>3</b>	89.7	82.3	27.3
				<b>6</b>	90.9	106.5	80.0
<b>No.1 F0</b> sample spiking with standard solution	7439 ± 0.22	8081 ± 1.03	14735 ± 0.46	<b>3</b>	82.7	112.4	244.3
				<b>6</b>	101.9	83.6	294.9
<b>No.1 F2</b> after passing through the column	0.39 ± 0.05	4.98 ± 0.22	7.65 ± 1.51	<b>3</b>	82.7	112.4	182.9
				<b>6</b>	101.9	83.6	128.7
<b>No.1 F4</b> after passing through the column	0.03 ± 0.01	8.07 ± 0.02	9.21 ± 1.12	<b>3</b>	88.3	108.1	76.7
				<b>6</b>	90.3	115.3	156.1
<b>No. 2</b>	0.64 ± 0.03	2.09 ± 0.19	11.14 ± 0.19	<b>3</b>	90.3	97.8	142.7
				<b>6</b>	87.5	103.3	162.9
<b>No.2 F0</b> sample spiking with standard solution	7754 ± 0.16	8090 ± 0.03	20397 ± 4.08	<b>3</b>	97.4	82.9	241.3
				<b>6</b>	81.9	93.4	199.2
<b>No.2 F2</b> after passing through the column	0.30 ± 0.05	2.58 ± 0.09	0.84 ± 0.00	<b>3</b>	96.9	89.5	169.0
				<b>6</b>	92.2	96.3	112.1

<sup>a</sup> Average value of two determination ± standard deviation

**Table 3.5** (Continued)

Sample	Found ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>			Add ( $\mu\text{g L}^{-1}$ )	Recovery (%)		
	Cadmium	Lead	Zinc		Cadmium	Lead	Zinc
No.2 F4 after passing through the column	0.32 ± 0.03	1.91 ± 0.14	7.59 ± 0.20	3	93.1	81.2	0.7
				6	85.3	101.3	103.5
No. 3	0.60 ± 0.05	4.92 ± 0.08	11.79 ± 0.34	3	95.9	107.4	57.4
				6	95.6	112.3	139.2
No.3 F0 sample spiking with standard solution	8869 ± 0.12	9667 ± 0.18	22121 ± 3.39	3	83.1	103.4	22.8
				6	96.9	104.1	108.8
No.3 F2 after passing through the column	1.01 ± 0.51	6.39 ± 0.41	11.23 ± 0.43	3	95.1	99.8	73.8
				6	88.1	82.4	374.9
No.3 F4 after passing through the column	0.09 ± 0.03	4.76 ± 0.20	8.33 ± 2.56	3	91.5	86.3	328.2
				6	90.3	93.2	273.5

<sup>a</sup> Average value of two determination ± standard deviation

In this work, we used the Chelex 100 resin column (the pictures of column are shown in appendix C) for treatment of water. The Chelex 100 is composed of iminodiacetate functional group and iminodiacetate ions as chelator for binding metal ions as shown in equation 1.10. Results on the removal efficiency of heavy metal ions in wastewater samples are shown in Table 3.6. The results showed that the Chelex 100 resin is very effective in binding metal ions. The percentage removal of the metal ions calculated for cadmium, lead and zinc were almost 100%.

**Table 3.6** Result for the removal efficiency of heavy metal ions in water treatment samples

Sample	Initial metal ions concentration <sup>a</sup> (mg L <sup>-1</sup> )			Removal efficiency (%)		
	Cadmium	Lead	Zinc	Cadmium	Lead	Zinc
No. 1	7.44 ± 0.22	8.08 ± 1.03	14.94 ± 0.46	100.0	99.9	99.9
				100.0	99.9	99.9
No. 2	7.75 ± 0.16	8.09 ± 0.03	20.40 ± 4.08	100.0	100.0	100.0
				100.0	100.0	100.0
No. 3	8.87 ± 0.12	9.67 ± 0.18	22.12 ± 3.39	100.0	99.9	99.9
				100.0	100.0	100.0

<sup>a</sup> Average value of two determinations ± standard deviation

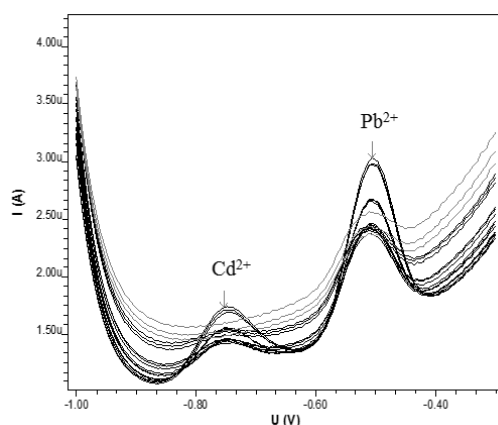
### 3.6 Application to ceramic ware samples

The proposed method was applied to the determination of some metal ions extracted from the surface of ceramic wares. Extraction of metals from glazed ceramic surface was carried out according to the standard method. The method extracted metals from the glaze by 4% (v/v) acetic acid, which the extracted solution can be applied directly as an electrolyte for simultaneous determination of cadmium and lead at trace levels by ASV using Bi-SPCE as a working electrode.

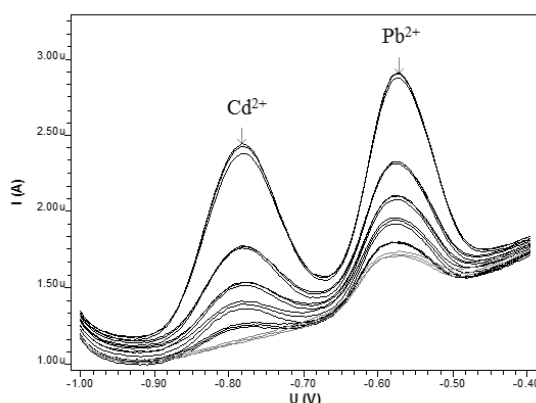
#### 3.6.1 Effect of pH of supporting electrolyte

The supporting electrolyte and pH can affect the voltammetric response of cadmium and lead when the Bi-SPCE was used as a working electrode. At trace

concentration level, the voltammograms of target metals in 4% (v/v) acetic acid solution (pH 2.3) was overlapped with the background signal as shown in Figure 3.14, while the voltammograms of target metals in 4% (v/v) acetic acid solution that has been adjusted pH to 4.5 were well defined peaks as shown in Figure 3.15. Therefore, the extracted sample solution was adjusted to pH 4.5 before the analysis because pH 4.5 suppressed the hydrogen evolution which was more pronounced in the acidic solutions (pH 2.3) [Lezi *et al.*, 2012] and in very low pH can occurring hydrogen gas from reduction of hydrogen ions in electrolyte solution that could damage the bismuth film.



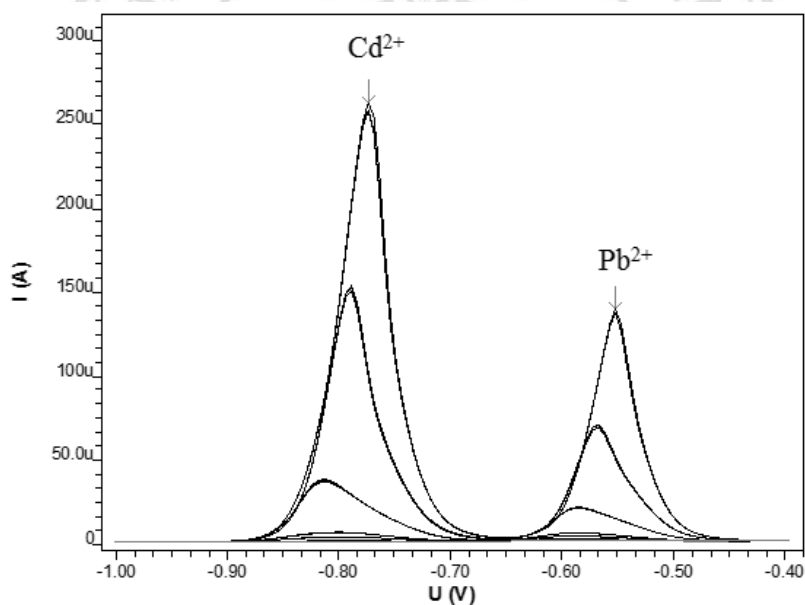
**Figure 3.14** Stripping voltammogram for cadmium and lead determination from 0.2 to 2.0  $\mu\text{g L}^{-1}$  at the Bi-SPCE modified with 0.4  $\text{mg L}^{-1}$  bismuth film in 4% (v/v) acetic acid (pH 2.3) and other condition are the same as in Table 3.1 (page 32)



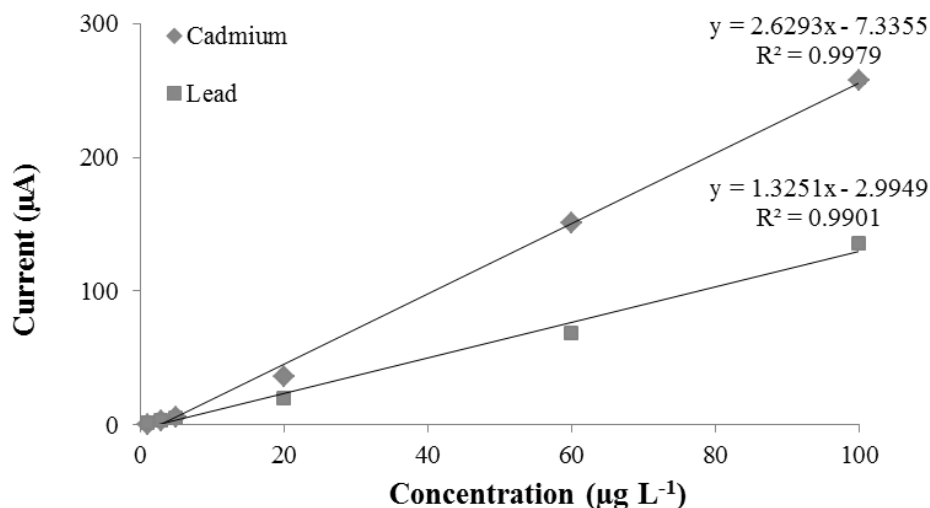
**Figure 3.15** Stripping voltammogram for cadmium and lead determination from 0.2 to 2.0  $\mu\text{g L}^{-1}$  at the Bi-SPCE modified with 0.4  $\text{mg L}^{-1}$  bismuth film in 4% (v/v) acetic acid (pH 4.5) and other condition are the same as in Table 3.1 (page 32)

### 3.6.2 Analytical characteristics

The analytical performance of the Bi-SPCE electrode was investigated by simultaneous analysis of cadmium and lead in concentration range from 1 to 100  $\mu\text{g L}^{-1}$  in 4% (v/v) acetic acid (pH 4.5) containing 0.4  $\text{mg L}^{-1}$  bismuth(III) solution. The square wave anodic stripping voltammetry response for different concentrations of heavy metal ions is illustrated in Figure 3.16. The corresponding calibration plots and correlation coefficients are  $y = 2.6293x - 7.3355$  and  $R^2 = 0.9979$  for cadmium, and  $y = 1.3251x - 2.9949$  and  $R^2 = 0.9901$  for lead (x: concentration ( $\mu\text{g L}^{-1}$ ), y: current ( $\mu\text{A}$ )) as shown in Figure 3.17. The limits of detection were 0.20  $\mu\text{g L}^{-1}$  for cadmium, and 0.11  $\mu\text{g L}^{-1}$  for lead. The results are given in appendix B.



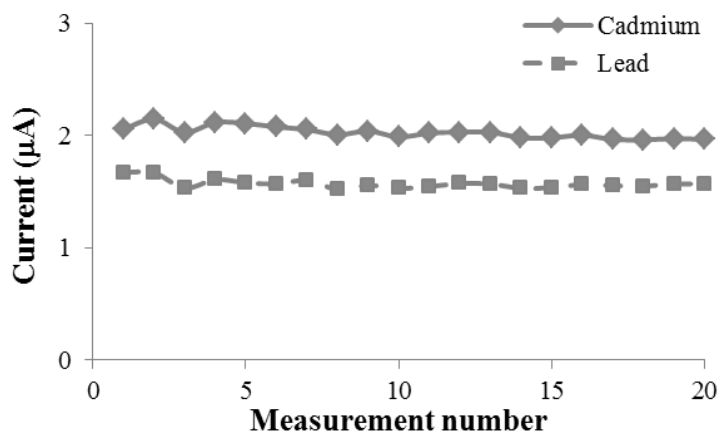
**Figure 3.16** The stripping voltammograms for various concentrations (1, 3, 5, 20, 60, and 100  $\mu\text{g L}^{-1}$ ) of cadmium and lead ions on the Bi-SPCE electrode and other condition are same as in Table 3.1 (page 32)



**Figure 3.17** The calibration graphs for the simultaneous analysis of cadmium and lead on the Bi-SPCE electrode, error bar: n=3 and other condition are same as in Table 3.1 (page 32)

### 3.6.4 Precision

A series of repetitive anodic stripping voltammetric measurements of  $2 \mu\text{g L}^{-1}$  of cadmium and lead in 4% (v/v) acetic acid (pH 4.5) were performed to further evaluate the stability of the Bi-SPCE electrode as shown in Figure 3.18. Good repeatability was evaluated from a relative standard deviation (RSD) for 20 replicates of 2.6% for both the metals on the same electrode.



**Figure 3.18** Signal stability for 20 repetitive measurements of cadmium and lead ( $2 \mu\text{g L}^{-1}$  each) in 4% (v/v) acetic acid solution (pH 4.5) on a single Bi-SPCE electrode and other condition are the same as in Table 3.1

### 3.6.5 Ceramic ware analysis

The proposed method was applied to the determination of some metals extracted from the surface of ceramic wares. Extraction of metals from glazed ceramic surface was carried out according to the standard method. First, ceramic sample was cleaned with detergent and dried in air. Then, it was filled by 4% (v/v) acetic acid in the sample to be tested for 24 h in dark location. After 24 h, the extracted solution was collected in plastic container for further voltammetric method determination of released metals. In this study, total concentrations of cadmium and lead released from ceramic ware samples by ASV on Bi-SPCE by standard addition method are shown in Table 3.7. It was found that the concentration of cadmium and lead released from ceramic ware samples are lower than the permissible values of the Thai industrial standard (The calculation are given in appendix D). Recovery obtained from spiking of the metal standard solution of 3 and 6  $\mu\text{g L}^{-1}$  into the extracted solution were found in the range of 80.4% to 109.6%.

**Table 3.7** Total concentrations of cadmium and lead released from ceramic ware samples by ASV on Bi-SPCE by standard addition method

Sample	Released amounts ( $\mu\text{g dm}^{-2}$ ) <sup>a</sup>		Add ( $\mu\text{g L}^{-1}$ )	Recovery (%)	
	Cadmium	Lead		Cadmium	Lead
No. 1	N.D.	0.179 ± 0.029	3	93.9	102.2
			6	88.7	90.6
No. 2	N.D.	0.194 ± 0.040	3	99.6	109.6
			6	88.2	103.4
No. 3	N.D.	0.185 ± 0.027	3	83.0	85.4
			6	98.6	85.5
No. 4	N.D.	0.208 ± 0.004	3	84.9	103.3
			6	80.4	98.6
No. 5	N.D.	0.237 ± 0.023	3	87.3	90.4
			6	84.5	95.1
No. 6	N.D.	0.125 ± 0.015	3	83.2	84.9
			6	100.2	96.9
No. 7	N.D.	0.334 ± 0.064	3	94.1	96.6
			6	82.3	87.9

<sup>a</sup> Average value of two determination ± standard deviation

N.D. mean not detected

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