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Sequential injection monosegmented flow voltammetric determination of cadmium and lead using a bismuth film working electrode

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ABSTRACT

A cost-effective sequential injection monosegmented flow analysis (SI-MSFA) with anodic stripping voltammetric (ASV) detection has been developed for determination of Cd(II) and Pb(II). The bismuth film working electrode (BiFE) was employed for accumulative preconcentration of the metals by applying a fixed potential of −1.10 V versus Ag/AgCl electrode for 90 s. The SI-MSFA provides a convenient means for preparation of a homogeneous solution zone containing sample in an acetate buffer electrolyte solution and Bi(III) solution for in situ plating of BiFE, ready for ASV measurement at a flow through thin layer electrochemical cell. Under the optimum conditions, linear calibration graphs in range of 10–100 $\mu g\,L^{-1}$ of both Cd(II) and Pb(II) were obtained with detection limits of 1.4 and 6.9 $\mu g\,L^{-1}$ of Cd(II) and Pb(II), respectively. Relative standard deviations were 2.7 and 3.1%, for 11 replicate analyses of 25 $\mu g\,L^{-1}$ Cd(II) and 25 $\mu g\,L^{-1}$ Pb(II), respectively. A sample throughput of 12 h^{-1} was achieved with low consumption of reagent and sample solutions. The system was successfully applied for analysis of water samples collected from a draining pond of zinc mining, validating by inductively coupled plasma-optical emission spectroscopy (ICP-OES) method.

1. Introduction

Heavy metals such as cadmium and lead are toxic, persistent pollutants and they can be bioaccumulated/concentrated through the food chain. Their contamination to the environment comes from different sources, e.g., soil erosion, mining and industrial activities. Therefore, the development of sufficiently sensitive, selective and reproducible analytical methods for precise and accurate determination of these metals at trace levels is essential. There are several techniques recently utilized including spectrometric, chromatographic and electroanalytical techniques. Spectrometric techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS) and atomic fluorescence spectrometry (AFS) although provide good sensitivity and selectivity, they usually involve expensive and large equipment.

Electroanalytical techniques such as stripping voltammetry on the other hand usually concern small instrument, which is relatively low cost, low power consumption and portable. The most widely used stripping voltammetric mode for determination of Cd(II) and Pb(II) is an anodic stripping voltammetry (ASV), which is conventionally performed on mercury electrode, e.g., hanging mercury drop electrode (HMDE) and mercury film electrode (MFE) [1]. Mercury electrode provides a wide cathodic potential limit for reduction of several metals and allows the formation of amalgams for accumulative preconcentration of the metals leading to very high sensitivity and reproducibility for ASV determination. However, due to toxicity of the mercury, recently mercury-free electrodes such as bismuth film electrode (BiFE) are extensively researched [2–32]. BiFE is environmentally friendly since the toxicity of bismuth and its salts is negligible. It can form "fused alloys" with heavy metals, analogously to the amalgams that mercury forms [4,11] leading to high sensitivity and reproducibility of the stripping signal and good resolution of the adjacent stripping peaks. Other attractive properties include its low background characteristics, wide alkaline pH working range and being partially insensitive to dissolved oxygen, which allows the analysis without the time-consuming de-oxygenation step [2,4–6,10,11]. Similar to the MFE, BiFE could be conveniently prepared by plating a thin bismuth film on a suitable substrate material, which can be done before (ex situ plating) [14] or at the same time (in situ plating) [8,9] with the deposition of the analyte metals. Various substrate materials could be used such as glassy carbon [2,5,6,20,25], carbon fiber [2,14], carbon paste [7,15,18], screen printed electrode [3,9,12,24,30], pencil lead [8], carbon nanotube [27], edged plane graphite [19], gold [16] and copper [17]. Other techniques for preparation of BiFE have been introduced such as sputtering of Bi film on silicon substrate to

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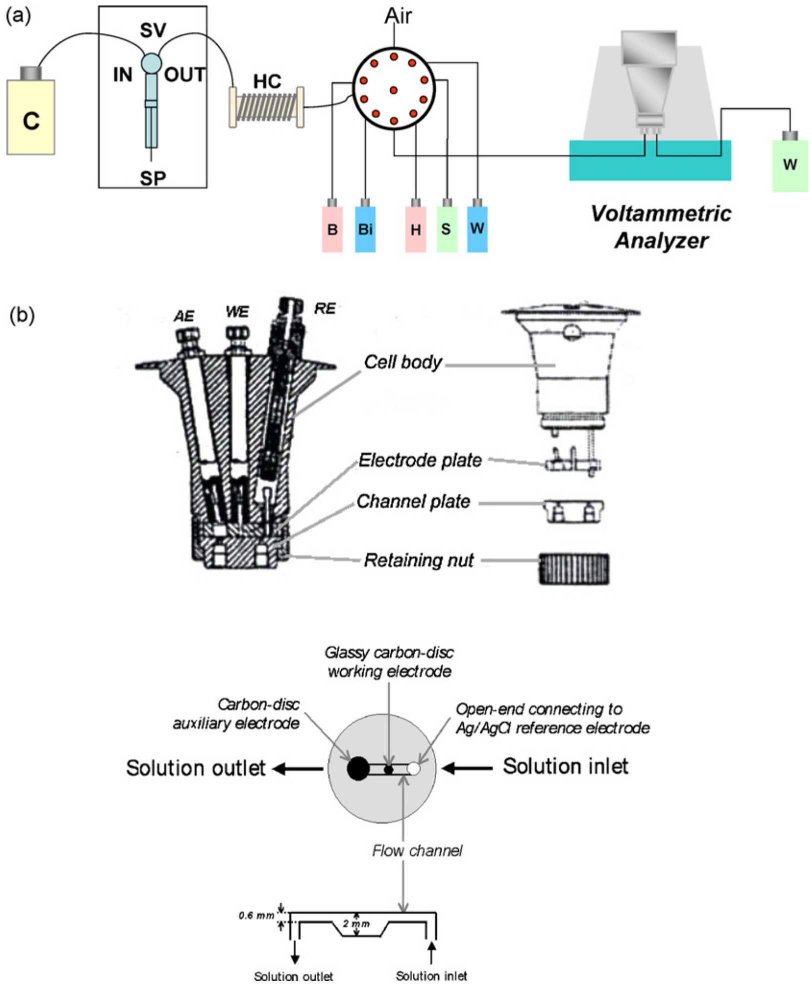


Fig. 1. The developed sequential injection anodic stripping voltammetric system. (a) Schematic diagram of the system, C: carrier (deionized water), SP: syringe pump, SV: switching valve, HC: holding coil, B: 0.2 M acetate buffer, Bi: 40 mg L^{-1} Bi(III) in 3 M acetate buffer, H: cleaning solution (0.1 M HNO_3), S: mixed metals standard/sample and W: waste. (b) A thin layer electrochemical flow-cell and the flow channel, AE: auxiliary electrode, WE: working electrode and RE: reference electrode.

produce BiFE microelectrode [22,23] and bismuth–carbon composite electrode using Bi nanoparticles [32]. BiFE is more mechanical durable than MFE which is suitable for application in flow systems [1,11]. Flow based analysis such as flow injection (FI) and sequential injection (SI) offers several advantages over batch analysis such as fast and higher degrees of automation, improvement of accuracy and precision, less risk of contamination and low consumption. Recently, several sequential injection systems have been developed for automation of ASV analysis [29–31,33–38]. However, most of them employing mercury electrodes, either HMDE [37,38] or MFE [34–36]. There is still lack of application of BiFE in flow system [11]. SI-ASV on Nafion® coated BiFE was developed for determination of Cd(II), Pb(II) and Zn(II) [29]. The hybrid FI/SI system using BiFE was also reported for ASV determination of Cd(II) and Pb(II), and AdSV determination of Co(II) and Ni(II) [30]. SI-ASV was proposed for determination of Cd(II), Pb(II) and Zn(II) employing an in situ plated bismuth film screen printed carbon electrode [31].

The SI with monosegmented flow analysis (MSFA) approach was introduced to promote good mixing of the solution zones sandwiched between two air segments, resulting from a turbulent flow in the monosegment [37,39,40]. This approach should improve efficiency in electrodeposition of metal ions on the working electrode, leading to high sensitivity and reproducibility of the analytical results. With MSFA sample dilution, single stock standard calibration and standard addition could be made in-line [37,40]. The SI-MSFA with voltammetric determination of atrazine on a HMDE was developed [37].

In this work, we developed a cost-effective SI system to perform MSFA aiming to gain benefit in convenient handling in solution preparation for in-line ASV determination of Cd(II) and Pb(II) employing an environmentally friendly BiFE as a working electrode. The BiFE was in situ plated on glassy carbon electrode and the same electrode could be repeatedly used for several times due to efficient cleaning in the flow system. The system provided sensitive and reproducible determinations of Cd(II) and Pb(II), with semi-automatic analysis and low chemical consumption. The developed system with new software offered opportunity to do complicated tasks in SIA, despite a simple script program has been used.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade. Deionized water (obtained from a system of Milli-Q, Millipore, Sweden) was used throughout. An acetate buffer solution (0.2 M, pH 4.6), which served as a supporting electrolyte was prepared by dissolving sodium acetate 3-hydrate (Ajax Finechem, Australia) (13.61 g) in water before adding of acetic acid (Carlo Erba, Italy) (5.7 mL) and making up to final volume of 500 mL with water. Working standard solutions of Pb(II) and Cd(II) were daily prepared by appropriate diluting the stock standard solutions (1000 mg L^{-1} atomic absorption standard solutions, Merck, Germany) with the acetate buffer solution. A stock solution of Bi(III) (1000 mg L^{-1}) was prepared by dissolving 0.23 g of bismuth (III) nitrate 5-hydrate (Carlo Erba, Italy) in 0.5 M HNO_3 solution. A Bi(III) plating solution (40 mg L^{-1}) was daily prepared by diluting the stock solution with 3 M acetate buffer solution.

2.2. Instrumentation and apparatus

An in-house assembled sequential injection-voltammetric system is depicted in Fig. 1(a). It consisted of a syringe pump (Cavro Model XL-3000, USA), a 10-port selection valve (Valco Instrument, USA), a voltammograph (VA 757, Metrohm, Switzerland). Tygon® tubing (1.25 mm i.d., 4.5 m long) was used for assembling a holding coil. Other flow lines were made of a PTFE tubing of 0.5 mm i.d. A thin layer cross-flow cell (Metrohm, Switzerland) as shown in Fig. 1(b) was employed for voltammetric measurement. It consisted of a glassy carbon disc working electrode (WE), a carbon disc auxiliary electrode (AE) and a Ag/AgCl (3 M KCl) reference electrode (RE). An in situ plated bismuth film electrode on the WE was used in anodic stripping voltammetric analysis. The system was computerized controlled by using a home-made program written in Visual Basic 6 (Microsoft, USA). Employing this controller program, different solution sequences as shown in Fig. 2 were created for investigation of monosegmented flow for efficient mixing of various solutions.

2.3. Procedure

The operational sequences for the determination of Pb(II) and Cd(II) by the SI-voltammetric system with monosegmented flow strategy are given in Table 1. This corresponds to the solution sequence F in Fig. 2. Before running the operational sequence, the "Start-up" program sequences was firstly executed, in order to fill the HC, the electrochemical cell and the tubing connecting to the port 6 of the selection valve with 0.2 M acetate buffer solution and to fill tubings connected to other ports of selection valve with their respective solutions. Then operational sequences were started as describing as follows (sequence F, Fig. 2). First, the acetate buffer solution (800 μL) was aspirated and then delivered through port 6 to the flow cell. Then, air (100 μL) was aspirated to separate buffer solution from the following solutions. After that, Bi(III) plating solution (Bi + B) and mixed standard/sample solution (M) were alternately aspirated to form stacked zones as shown in Fig. 2(F). Then selection valve was switched to port 1 to perform flow reversal to promote mixing of the stacked zones together [39], by aspirating air (300 μL) and pushing air and 25 μL of the solution to waste (port 2). The mixing zone was then propelled through a cross-flow cell for electrodeposition of the metals by applying a potential of −1.10 V versus Ag/AgCl to the WE for a specified deposition time. The air segment at the back was taken out to waste before buffer solution was sent to the flow cell. Then, the stripping step was performed in a medium of acetate buffer electrolyte under stop flow condition. A voltammogram was recorded using the following condition: sweep mode, square wave; sweep potential, −1.10 to 0.20 V; sweep rate, 0.50 V/s. Finally, the flow cell and the electrodes were cleaned by flowing cleaning solution (0.1 M HNO_3) through the flow cell while applying a potential of 0.20 V to the WE.

3. Results and discussion

3.1. Development of SI system and software for SI operation

An SI system was assembled from commercially available OEM components in order to make the system to be cost-effective. Control of the pump and selection valve was accomplished by sending an ASCII code to the respective component via computer serial ports (COM port). An in-house developed software for control of the SI system was designed and written in Visual Basic 6.0. The control panel of the software is depicted in Fig. 3. As can be seen from the figure, the component could be controlled manually by clicking on the button on the screen or automatically by creating a program sequences or a script program. The way of writing a script program was convenient, i.e., by typing a value in a parameter box of each component and then click "Add" button to insert a script line in the Program Control box. The program script could be easily edited by highlighting on the line to be deleted or inserted and then clicking "Remove" or "Add" button, accordingly. Instruction for delay and

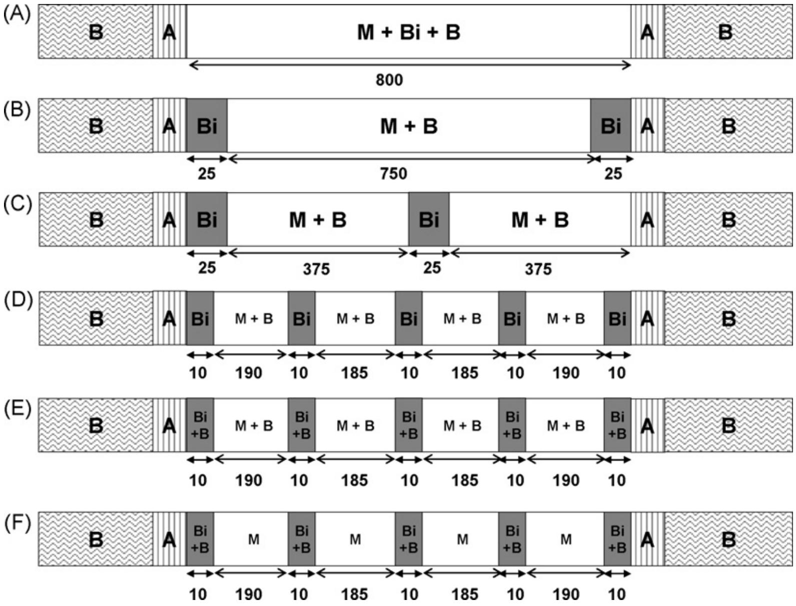


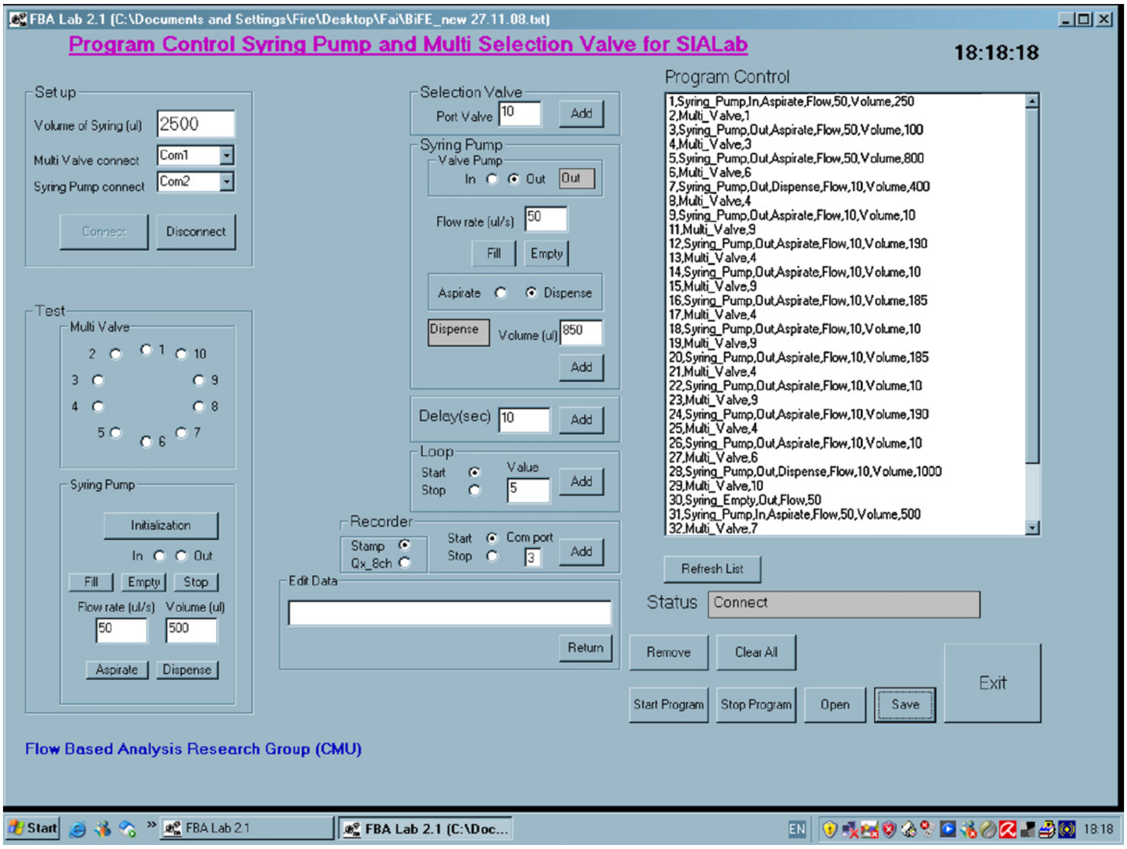
Fig. 2. Sequence of solutions in the monosegmented zone before mixing; A: air, M: mixed solution of Cd(II), Pb(II) and Zn(II) standards (0.1 mg L^{-1} each), Bi: 40 mg L^{-1} Bi (III) in nitric acid (pH 1.7), B: 0.2 M acetate buffer, Bi + B: 40 mg L^{-1} Bi (III) in 3 M acetate buffer. Volume of solution indicated under each zone is in microliter.

Table 1
Operational sequences of the SI-MSFA–ASV method for determination of Cd(II) and Pb(II).

Step	Description	Pump valve position	Selection valve position	Volume (μL)	Flow rate (μLs^{-1})	WE potential (V)
1	Load buffer solution	Out	3	800	50	
2	Deliver carrier solution to flow cell	Out	6	400	10	
3	Load air	Out	1	100	50	
4	Load bismuth plating solution	Out	4	10	10	
5	Load standard/sample	Out	9	190	10	
6	Load bismuth plating solution	Out	4	10	10	
7	Load standard/sample	Out	9	185	10	
8	Load bismuth plating solution	Out	4	10	10	
9	Load standard/sample	Out	9	185	10	
10	Load bismuth plating solution	Out	4	10	10	
11	Load standard/sample	Out	9	190	10	
12	Load bismuth plating solution	Out	4	10	10	
13	Load air	Out	1	300	50	
14	Taken air out	Out	10	325	50	
15	Deley time 5 s for clicking on start button of the voltammograph					
16	Deliver the sample zone through flow cell for deposition step	Out	6	750	10	−1.10
17	Taken air out	Out	10	150	100	
18	Push buffer to flow cell	Out	6	200	10	
19	Stripping and recording of voltammogram	Out				−1.10 to 0.20
20	Load cleaning solution	Out	7	700	50	
21	Load carrier	In		100	50	
22	Deliver zone of cleaning solution to strip bismuth film	Out	6	975	50	0.20

loop control could be inserted similarly. Additionally, the software was prepared for control of components which will be used in other applications or further development of the system to higher automation, e.g., peristaltic pump, recorder and auto-sampler.

Using the developed system, sequential injection monosegmented flow voltammetric analysis could be semi-automatically performed according to the operational sequences as described in Table 1. The script program was started to run by clicking on “Start Program” button and it can be stopped at any time by clicking “Stop Program” button. The complicated procedure could be done with higher degrees of automation employing the developed system as described in Section 2.3.



FBA Lab 2.1 (C:\Documents and Settings\Fire\Desktop\Fai\BiFE_new 27.11.08.txt)

Program Control Syring Pump and Multi Selection Valve for SIALab

18:18:18

Volume of Syring (ul) 2500
Multi Valve connect Com1
Syring Pump connect Com2
Port Valve 10
Valve Pump In ○ ● Out Out
Flow rate (ul/s) 50
Aspirate ○ ● Dispense
Volume (ul) 850
Delay(sec) 10
Loop Start ● Stop ○ Value 5
Recorder Stamp ● Qx_8ch ○ Start ● Stop ○ Com port 3
Test Syring Pump In ○ ○ Out Flow rate (ul/s) 50 Volume (ul) 500

Program Control

```
1,Syring_Pump,In,Aspirate,Flow,50,Volume,250
2,Multi_Valve,1
3,Syring_Pump,Out,Aspirate,Flow,50,Volume,100
4,Multi_Valve,3
5,Syring_Pump,Out,Aspirate,Flow,50,Volume,800
6,Multi_Valve,6
7,Syring_Pump,Out,Dispense,Flow,10,Volume,400
8,Multi_Valve,4
9,Syring_Pump,Out,Aspirate,Flow,10,Volume,10
11,Multi_Valve,9
12,Syring_Pump,Out,Aspirate,Flow,10,Volume,190
13,Multi_Valve,4
14,Syring_Pump,Out,Aspirate,Flow,10,Volume,10
15,Multi_Valve,9
16,Syring_Pump,Out,Aspirate,Flow,10,Volume,185
17,Multi_Valve,4
18,Syring_Pump,Out,Aspirate,Flow,10,Volume,10
19,Multi_Valve,9
20,Syring_Pump,Out,Aspirate,Flow,10,Volume,185
21,Multi_Valve,4
22,Syring_Pump,Out,Aspirate,Flow,10,Volume,10
23,Multi_Valve,9
24,Syring_Pump,Out,Aspirate,Flow,10,Volume,190
25,Multi_Valve,4
26,Syring_Pump,Out,Aspirate,Flow,10,Volume,10
27,Multi_Valve,6
28,Syring_Pump,Out,Dispense,Flow,10,Volume,1000
29,Multi_Valve,10
30,Syring_Empty,Out,Flow,50
31,Syring_Pump,In,Aspirate,Flow,50,Volume,500
32,Multi_Valve,7
```

Status Connect

Fig. 3. The control-panel page of an in-house SI controller software (for details see text).

3.2. Optimization of experimental conditions

Conditions of the square wave anodic stripping voltammetric analysis for determination of cadmium and lead (as described in Section 2.3) was selected from the previous study [35], except bismuth film electrode (BiFE) was used instead of mercury film electrode in order to avoid the use of toxic mercury. Preparation of BiFE could be done either by ex situ plating (preplating) or in situ plating. In situ plating could be more convenient to perform by off-line spiking of the standard/sample solution with Bi(III) solution and formation of bismuth film simultaneously occurred with the analyte metals accumulation during the deposition step. In this work, a monosegmented flow analysis (MSFA) [37,39,40] approach was applied in SI systems in order to provide good mixing of Bi(III), standard/sample and acetate buffer electrolyte solutions together in a monosegmented zone. This could be carried out by using air plugs to sandwich the solution zones, which prevent dispersion of solution into a carrier stream and the turbulent flow occurring in the air segmented zone would promote mixing of the sandwiched solution zones to form a homogenized monosegmented zone. The homogeneous solution would provide good performance and reproducibility in the deposition and stripping steps of ASV analysis because the concentration gradient of the sample zone entering the electrochemical flow cell would less occur while the potential was applied to the working electrode [37]. Other segmented flow could also be used to promote mixing but complicated instrumentation and procedure may be needed, e.g., air segmentor and bubble remover devices are required. A 0.2 M acetate buffer pH 4.6 was selected as a supporting electrolyte for voltammetric analysis because this medium provided wider potential window of BiFE than the more acidic medium [5].

Preliminary investigation on the effect of Bi(III) concentration used for formation of BiFE on sensitivity of metals determination was carried out by the off-line premixing of solutions of metal ions, Bi(III) and acetate buffer. The final solution contained 0.01 and 0.1 mg L^{-1} each of Cd(II), Pb(II) and Zn(II), 0.2 M acetate buffer and different concentrations of Bi(III). The premixed solution (800 μL) was aspirated to sandwich in between air plugs and 0.2 M acetate buffer as shown in Fig. 2(A). After flow reversal, the air plug was removed and the solution zone was then pushed to the flow cell. A fixed potential of −1.10 V versus Ag/AgCl electrode was applied to the WE while the solution zone was propelled at 10 μLs^{-1} through the cell. The stripping was performed in a medium of 0.2 M acetate buffer by scanning potential from −1.10 to 0.20 V. Effect of Bi(III) concentration on peak currents of the analyte metals is illustrated in Fig. 4. It was found that peak current sharply increased with the increase of Bi(III) concentration and reached the maximum at about 2.5 mg L^{-1} Bi(III). This is the same trend with the peak current of Bi itself. Bi(III) concentration would dictate the thickness of the Bi film for deposition of the analyte metals. At high Bi(III) concentration the metals may difficultly stripped out from a thick Bi film leading to lower peak current and broader peak. The Bi(III) concentration of 2.5 mg L^{-1} was selected for further experiment. The in situ plated BiFE on GCE should provide advantages in term of simplicity, low cost and convenient operation since the same electrode could be repeatedly used after proper cleaning.

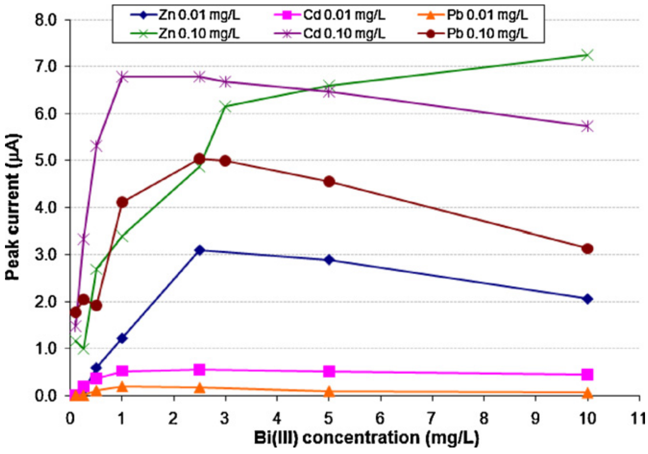


Fig. 4. Effect of concentration of Bi(III) plating solution on peak current of the analyte metals (for details see text).

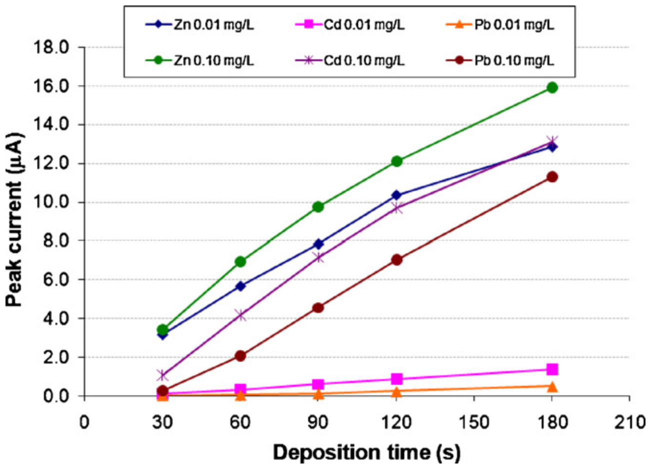


Fig. 5. Effect of deposition time on peak current of the analyte metals (for details see text).

The reproducibility of peak current may depend on the cleanliness of the working electrode. The cleaning step was applied after the voltammogram was recorded by flowing a cleaning solution (0.1 M HNO_3) while the potential of WE was held at +0.20 V for 15 s. It was found that the relative standard deviations for seven consecutive determinations of 50 μg L^{-1} Cd(II) and Pb(II) were improved from 5.9 and 6.9 to 1.8 and 1.3%, respectively, for 0 s and 15 s cleaning time. Flow system helped cleaning the working electrode better than in batch method because the fresh solution was flowed through the electrode during cleaning. This would lead to repeatedly use of BiFE on GCE with better reproducibility than in batch method.

Deposition time and volume of the sample zone passing though the flow cell during deposition step were investigated by aspirating different volumes (200, 500, 800, 1100 and 1700 μL of the premixed solution), which corresponded to deposition time of 30, 60, 90, 120 and 180 s, respectively. Effect of deposition time on peak currents of 0.01 and 0.10 mg L^{-1} of each metal is depicted in Fig. 5. Roughly, peak currents linearly increased with deposition time up to 120 s. Deposition time of 90 s was chosen in order to compromise between sample throughput and sensitivity.

Effect of sequence of different solutions (standard/sample, buffer and Bi(III)) on the homogenization of the mixture zone in a monosegment was investigated by creating a monosegment of 800 μL total volume by using different sequences of solutions as depicted in Fig. 2. Once the sequence was created, the stacked zones were moved forward and backward to cause turbulent mixing of the stacked zones in the monosegment. A sequence of off-line mixed (premixed) solution as shown in Fig. 2(A) was also carried out for comparison. A plating solution (40 mg L^{-1} Bi(III)) used in sequences A–D was prepared in water, while those of sequences E and F was prepared in 3 M acetate buffer. The peak currents obtained for 0.10 mg L^{-1} each of Cd(II), Pb(II) and Zn(II) and for Bi(III) when using different sequences are shown in Fig. 6. It was found that all sequences gave comparable peak currents for all the metals.

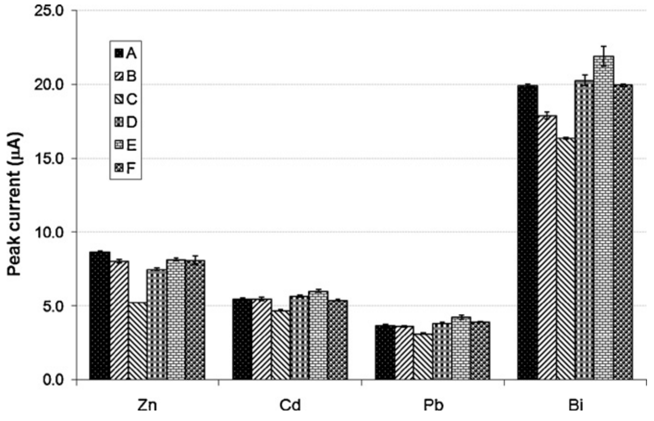


Fig. 6. Peak currents of metals obtained from different sequences A–F as shown in Fig. 5 (for details see text).

However, sequence E, which should provide better mixing and thus resulted in highest peak currents. Sequence E was modified to be sequence F by employing standard/sample solution without off-line adding of buffer, in order to simplify the sample preparation procedure. This modification resulted in a little bit lower peak currents of the metals, but with better reproducibility. The sequence F was selected for sample analysis. Thanks to the automation of the developed SIA system, this complicated procedure could be easily performed with using a simple script program.

3.3. *Analytical features of the proposed system*

Using SI-monosegmented flow of sequence F together with the conditions as described in Section 2.3, calibration graphs of Cd(II), Pb(II) and Zn(II) in range of 10–100 µg L^{-1} of each metal were constructed by plotting peak current (µA) versus concentration of metal ions (µg L^{-1}). Fig. 7 shows a series of voltammograms. It could be seen that for Zn(II) a good linear calibration could not be obtained yet. Further studies should be needed for the determination of zinc. Under the selected conditions, linear calibration graphs could be obtained for Cd (II) and Pb(II) with the calibration equations, $y = 0.0551x - 0.1142$; $R^2 = 0.9999$ for Cd(II) and $y = 0.0506x - 0.5435$; $R^2 = 0.9966$ for Pb(II). The detection limits (the concentration corresponding to three times of standard deviation of blank) were obtained at 1.4 µg L^{-1} for Cd(II) and 6.9 µg L^{-1} for Pb(II) for deposition time of 90 s. The relative standard deviations for 11 replicate analyses of 25 µg L^{-1} Cd(II) and 25 µg L^{-1} Pb(II) were 2.7 and 3.1%, respectively. The analysis time for one sample is 5 min (sample throughput of 12 h^{-1}). Each analysis cycle consumed 750 µL of sample, 50 µL of 40 mg L^{-1} Bi(III) plating solution and 800 µL of 0.2 M acetate buffer solution.

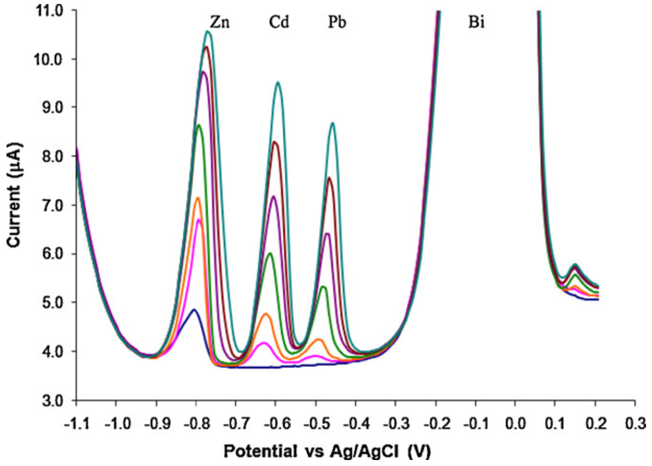


Fig. 7. Voltammograms of standard solutions containing Zn(II), Cd(II), Pb(II) obtained from SI-MSFA–ASV on BiFE; concentrations of each metal from bottom to top: 0.0, 10.0, 20.0, 40.0, 60.0, 80.0 and 100.0 µg L^{-1}.

Table 2

Concentrations of Cd(II) and Pb(II) in water samples found by SI-monosegmented flow–ASV and ICP-OES methods.

Sample	Concentration of metals found (mg L^{-1}) by			
	SI-ASV		ICP-OES	
	Cd	Pb	Cd	Pb
1	0.56 ± 0.02	3.20 ± 0.02	0.51 ± 0.02	3.02 ± 0.06
2	0.78 ± 0.02	2.10 ± 0.04	0.73 ± 0.04	2.01 ± 0.03
3	0.56 ± 0.01	2.69 ± 0.02	0.52 ± 0.02	2.52 ± 0.04
4	0.23 ± 0.01	3.62 ± 0.00	0.21 ± 0.02	3.54 ± 0.05
5	0.36 ± 0.00	3.85 ± 0.00	0.34 ± 0.03	4.02 ± 0.06
6	0.44 ± 0.00	2.55 ± 0.00	0.43 ± 0.03	2.53 ± 0.04
7	0.84 ± 0.02	1.30 ± 0.02	0.82 ± 0.04	1.22 ± 0.02
8	0.57 ± 0.01	2.11 ± 0.02	0.51 ± 0.02	2.03 ± 0.05
9	0.76 ± 0.01	1.40 ± 0.03	0.82 ± 0.03	1.52 ± 0.04
10	0.34 ± 0.07	3.32 ± 0.06	0.31 ± 0.02	3.52 ± 0.05

Monosegmented flow provides completed mixing of the solution zones, thus it would open possibility to perform in-line single standard calibration and in-line standard addition procedures. Preliminary experiment was carried out for in-line single standard calibration by varying the volume of the mixed metals standard to be aspirated into the monosegmented zone. Linear calibration graphs were obtained: $y = 0.0110x - 0.0525$; $R^2 = 0.9996$ for Cd(II) and $y = 0.0701x - 0.6285$; $R^2 = 0.9994$ for Pb(II). However, more investigations and refinement for the optimum condition should be made further.

3.4. *Analysis of real samples*

The proposed system was employed for determination of Cd(II) and Pb(II) in surface water samples collected from a draining pond of zinc mining in northern Thailand. Such a sample was collected in a clean polyethylene bottle (1 L) with adding of HCl to acidify sample to about pH 1. No sample pretreatment was made except filtering of the sample just before the analysis and dilution of sample with water (10-fold dilution for Cd(II) and 40-fold dilution for Pb(II) determinations). Samples were also analyzed by ICP-OES at the Office of Primary Industry and Mine Region 3, Chiang Mai for comparison. The obtained results are presented in Table 2. According to *t*-test at 95% confident limit, the results obtained from both the methods were in good agreement ($t_{\text{critical}} = 2.26$, $t_{\text{calculate}} = 0.26$ and 0.05 for Cd(II) and Pb(II), respectively). The results were correlated each other well (SI = 0.9463 ICP + 0.0522, $R^2 = 0.9761$ for Cd(II) and SI = 0.9512 ICP + 0.1472, $R^2 = 0.9784$ for Pb(II)). The system was also tried for analysis of bottled mineral drinking water. Concentration of Cd(II) and Pb(II) in those samples were below detection limit of the method. By spiking 25 and 50 µg L^{-1} of both metal ions into a sample, recoveries were found in range of 95–108% for Cd(II) and 100–115% for Pb(II). Application of the developed system to determination lower concentration of metal ions in water samples nearby the mining area will be further investigated.

4. Conclusion

A cost-effective sequential injection system was assembled and applied for monosegmented flow anodic stripping voltammetric determination of Cd(II) and Pb(II) employing BiFE in situ plating on a glassy carbon working electrode. The system offered non-toxic, convenient, high degrees of automation and low consumption in the analysis, with precise and accurate results for the determination of Cd(II) and Pb(II) in contaminated water samples. The monosegmented flow help in in-line preparation of homogeneous solution mixture of sample, Bi(III) plating solution and acetate buffer supporting electrolyte solution. The system has high potential to be developed further to be automated. Further investigations for in-line dilution, in-line single standard calibration and in-line standard addition procedures employing monosegmented flow approach are in progress.

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