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On-line preconcentration and determination of lead and cadmium by sequential injection/anodic stripping voltammetry

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ABSTRACT

The highly sensitive determination of lead (Pb(II)) and cadmium (Cd(II)) ions, with a limit of detection of 0.01 $\mu g\,L^{-1}$ for Pb(II) and Cd(II), by on-line preconcentration and anodic stripping voltammetry (ASV) controlled by a sequential injection analysis (SIA) system is reported here. The SIA system consisted of a syringe pump, an 8-port selection valve and a 6-port switching valve and was incorporated with a bismuth coated screen-printed carbon nanotube electrode (Bi-SPCNTE). The preconcentration of metal ions was performed by solid phase extraction using an Analig TE-05 chelating resin mini-column on a switching valve. The metal ions collected were then eluted from the resin with 1 M hydrochloric acid (HCl), deposited on the electrode surface at −1.3 V vs. Ag/AgCl and then measured with ASV. The pH of the sample, eluent volume, flow rate, concentration of the bismuth plating solution and the square-wave voltammetric parameters were optimized. Under the optimum conditions, an enrichment factor of 11.9-fold and 6.6-fold for Pb(II) and Cd(II) ions, respectively, was attained. Detection of Pb(II) and Cd(II) had two different linear ranges (0.5–15 $\mu g\,L^{-1}$ and 15–70 $\mu g\,L^{-1}$).

1. Introduction

The contamination of the environment by heavy metals remains a serious problem because of their non-biodegradability and high toxicity, yet their continued exposure in the environment from mining, natural sources and enrichment and release from human technological uses. The toxic heavy metals are incorporated into water and various food chains where they can gain entry into, for example, human bodies via food, drinking water and breathing airborne particles. Therefore, a highly sensitive method for the detection and quantification of trace heavy metals is required. Several different techniques are available for heavy metal determination, such as atomic absorption spectroscopy (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), and anodic stripping voltammetry (ASV). ASV is the most attractive electrochemical technique for the determination of trace heavy metals due to its high sensitivity and selectivity. Namely, the electrodeposition of target metals from the solution onto/into the working electrode of an electrochemical cell and subsequent stripping of the deposited metals provides the most sensitive strategy for the determination of trace metals [1]. An additional advantage of ASV over the other three methods (AAS, ICP-AES or ICP-MS) is the simplicity of the required instrumentation, which is relatively inexpensive, low electrical power consumption, portable as well as suitable for automation [2–5]. Combination systems between flow-based techniques, including flow-injection analysis (FIA) and sequential injection analysis (SIA), and ASV have been used in analytical chemistry during the last three decades [6,7]. SIA allows ASV to be performed with high precision because of the excellent reproducibility of the mixing conditions and mass transport between the electrode surface and the flowing stream solution [8]. Moreover, SIA is currently viewed as a powerful analytical technique for automated sample pretreatment and trace-level assays [9,10].

Carbon nanotubes (CNTs) have been shown to possess a good potential for heavy metal analysis due to their high electrical conductivity, high surface area, significant mechanical strength

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and good chemical stability. Therefore, the fabrication of screen-printed carbon nanotube electrodes (SPCNTE) is attractive. In an effort to improve the sensitivity of heavy metal detection by electrochemical analysis, bismuth (Bi) coated screen-printed carbon nanotube electrodes (Bi-SPCNTEs) have been used as the working electrode in batch analysis [11,12]. Recently, Injang et al. reported an automation method with SIA using Bi-SPCNTE [13]. Although Bi-SPCNTE provides a very high sensitivity the anodic signal from Bi-SPCNTE can easily be disturbed by the presence of other interfering cations and anions in real samples. Solid phase extraction (SPE) is a common sample preparation method for simultaneously removing interfering compounds and preconcentrating the sample. However, SPE consists of sophisticated procedure which is the major cause of low precision and accuracy in the results. Hence, in this work, Bi-SPCNTE was incorporated with on-line preconcentration system to perform highly sensitive, precise, accurate and automated determination of trace heavy metals in real world samples.

The aim of the present work was to develop a highly sensitive automated method for the simultaneous determination of Pb(II) and Cd(II) ions at ultratrace levels by incorporation of on-line preconcentration using SIA/ASV at Bi-SPCNTE. The developed method was successfully applied for determination of trace levels of Pb(II) and Cd(II) in drinking water, pond water, tap water, green tea, soup, fish and cockles.

2. Experimental

2.1. Chemicals and reagents

All standard and reagent solutions were prepared with standard and analytical grade reagents using ultrapure water (resistivity$\geq$18.2 MΩ cm^{-1}) from a Milli-Q Ultrapure Water Purification System (Millipore, USA). The working standard solutions of Pb(II) and Cd(II) were prepared daily by the appropriate dilution of the stock standard solutions (1,000 mg L^{-1} atomic absorption analysis standard solution, BDH Chemicals, England) with 1 M hydrochloric acid (HCl) solution. A 1,000 μg L^{-1} Bi(III) plating solution was prepared by the appropriate dilution of the stock solution of Bi(III) (1,000 mg L^{-1} atomic absorption analysis standard solution, Merck, Germany) with 1 M HCl solution. The 1 M HCl, which served as an eluent, a supporting electrolyte and an electrode cleaning solution, was prepared by the appropriate dilution of HCl (analytical grade, 37%, 1.19 g mL^{-1}, Merck, Germany). Sodium acetate trihydrate (analytical grade, Fluka Chemika, Switzerland), concentrated acetic acid (analytical grade, 100%, Merck, Germany) and 3 M HCl solution were used to make the 0.1 M acetate buffers of the desired pH. In order to prevent metal contamination, laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution prepared by dilution of concentrated nitric acid (analytical grade, 65%, Merck, Germany). Multi-walled CNTs were obtained from Nanomaterials Research Unit (Chiangmai University, Thailand). Prior to use, the CNTs were treated in a mixture of concentrated sulfuric acid (analytical grade, 95–97%, 1.84 g mL^{-1}, Merck, Germany) and concentrated nitric acid. One hundred milligrams of macrocyclic chelating solid support material, Analig TE-05 (60–100 mesh, IBC Advanced Technologies, USA), was packed in a mini-column (2 mm i.d. and 4.5 cm length).

2.2. Electrode preparation

Prior to use, CNTs were functionalized by dispersing 1.0 g of CNTs in 50 mL of a 3:2 (v/v) ratio of concentrated H_2SO_4: HNO_3 and the mixture was then agitated by ultrasonic wave for 12 h. After that, the CNT suspension was washed with Milli-Q water until the pH of the mixture approached 7, filtered and dried at 80 °C [13–16].

SPCNTEs were prepared in house by mixing the functionalized CNTs with carbon ink (Electrodag PF-407C, Acheson, USA) and screen-printing on PVC substrates using silver ink (Electrodag 7019, Acheson, USA) as a conductive pad. Bi-SPCNTEs were prepared by on-line in situ plating as previously reported [13].

The screen-printed carbon electrodes (SPCEs) were prepared in house using carbon ink (Electrodag PF-407C, Acheson, USA), silver ink (Electrodag 7019, Acheson, USA) and PVC substrates. Bi film SPCEs (Bi-SPCEs) were prepared by on-line in situ plating [13,14].

2.3. Apparatus

The SIA system for on-line preconcentration and determination of Pb(II) and Cd(II) (MGC Auto-Pret MP-014S, MGC, Japan), consisted of a 3-way syringe pump, an 8-port selection valve and a 6-port switching valve. A mini-column of the Analig TE-05 chelating resin was installed on a switching valve. PTFE tubing was used for flow lines (0.8 mm i.d.) and a holding coil (1.5 mm i.d.). The system was computer controlled using controlling program MGC LMPro ver.2.5.

ASV was carried out in a thin-layer flow cell (Bioanalytical Systems, USA) using an eDAQ Potentiostat (eDAQ, Australia). The thin-layer flow cell consisted of SPCNTE as the working electrode, a gasket as a spacer, an Ag/AgCl (3 M KCl) reference electrode, and a stainless steel tube as both the counter electrode and solution outlet of the flow cell. The electrochemical experiments were housed in a Faraday cage to prevent electrical noise.

2.4. Procedure

The step sequence method for the preconcentration and determination of Pb(II) and Cd(II) ion levels using the SIA/ASV system (schematically shown in Fig. 1) is shown in Table 1.

Firstly, the switching valve was set to the loading stage and 1 mL of 1 M HCl was aspirated via the selection valve into the holding coil, and then dispensed in the reverse direction through the mini-column, followed by 1 mL of ultrapure water for cleaning the column (step 1). Secondly, 1.5 mL of a 0.1 M acetate buffer of the appropriate pH was aspirated and dispensed into the mini-column for column conditioning (step 2). Thirdly, 3 mL of a sample solution, which was adjusted to the appropriate pH, was aspirated and introduced into the mini-column (step 3) for preconcentration and separation of the sample matrices. This sample loading step was repeated two times to introduce a total sample volume of 6 mL and then 0.6 mL of acetate buffer was aspirated and dispensed for washing of matrices and interferences (step 4). After that, 0.6 mL of a Bi(III) plating solution was aspirated and dispensed into the thin-layer flow cell in which the Bi(III) was electrodeposited on the electrode at −1.3 V vs. Ag/AgCl to form a Bi film (step 5). After the switching valve was turned to the eluting stage, 0.72 mL of 1 M HCl was aspirated and dispensed to elute collected metal ions in the mini-column. When the eluate containing analytes flowed into the thin-layer flow cell, the metal ions were deposited on the Bi coated electrode at −1.3 V vs. Ag/AgCl. In order to increase the sensitivity, 0.12 mL of the eluate concentrated with analyte metal ions was aspirated in the reverse direction and dispensed into the thin-layer flow cell again (step 6). Then the flow of the solution was stopped for a 15 s equilibration time (step 7). For the detection step, the voltammogram was recorded from −1.2 to 0.3 V vs. Ag/AgCl by scanning a potential in the square-wave waveform with 75 Hz frequency, 4 mV step potential, and 50 mV pulse amplitude (step 8). Finally, the switching valve was set to the loading stage, and 3 mL of 1 M HCl was aspirated and dispensed into the thin-layer flow cell

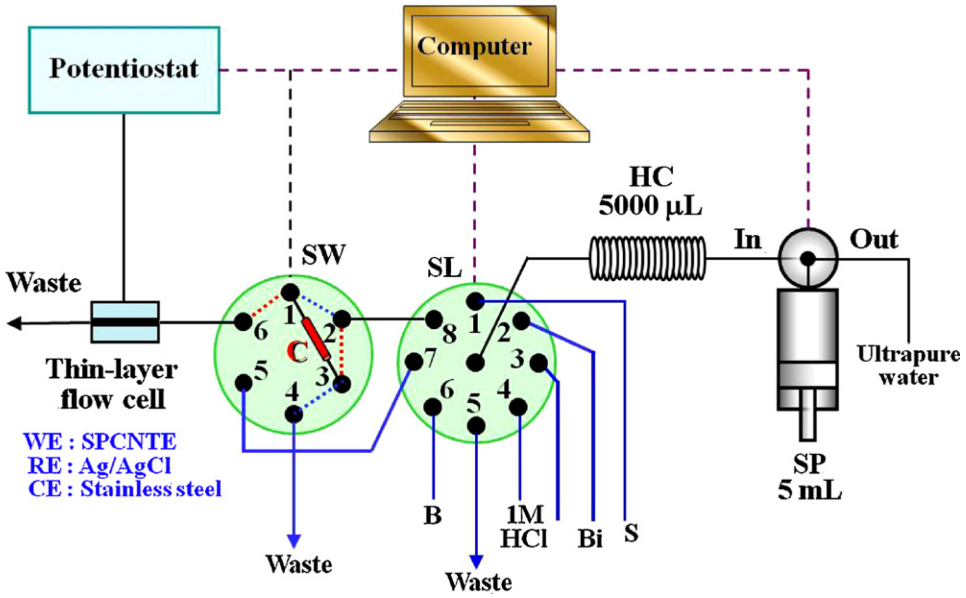

Fig. 1. Schematic diagram of the SIA/ASV system for preconcentration and determination of Pb(II) and Cd(II). SP, Syringe pump; SL, selection valve; SW, switching valve; HC, holding coil; C, mini-column of chelating resin; B, 0.1 M acetate buffer (pH 3); 1 M HCl, eluent and electrode cleaning solution; Bi, Bi(III) plating solution; S, sample solution; WE, working electrode (SPCNTE); RE, reference electrode (Ag/AgCl, 3 M KCl); CE, counter electrode (stainless steel).

to clean the electrode from residual analyte metals and Bi film at +0.3 V vs. Ag/AgCl (step 9).

3. Results and discussion

3.1. Electrochemical responses of SPCNTE and SPCE

In this work, the CNT electrodes were fabricated by mixing the functionalized multi-walled CNTs, carbon ink and solvent and screen-printing on PVC substrates because they are inexpensive, simple and suitable for several electroanalytical techniques. To investigate the performance of the working electrode, a SPCE was also used as the working electrode in the comparative study with the SPCNTE. Representative square-wave anodic stripping voltammograms of a solution containing 50 $\mu g\,L^{-1}$ Pb(II) and Cd(II) ions at in situ plated Bi-SPCNTE and Bi-SPCE are shown in Fig. 2, where the analytical signals of Bi-SPCNTE were clearly higher than that obtained with Bi-SPCE.

3.2. Examination of the preconcentration procedure

The preconcentration procedure, that is the sample loading, washing and elution from the Analig TE-05 chelating resin mini-column, was studied by on-line preconcentration followed by ASV detection.

Table 1
Step sequence protocol for the preconcentration method for the determination of Pb(II) and Cd(II) ions using the SIA/ASV system.

Step	Operating description	Volume (µL)	Flow rate ($\mu L\,s^{-1}$)	Syringe valve position	Syringe pump status	Valve position		Electrode potential (V)
						SL	SW	
(1) Column cleaning	(a) 1 M HCl	1000	200	In	Aspirate	4	Load	
	(b) Cleaning	1000	25	In	Dispense	8	Load	
	(c) Ultrapure water	1000	200	Out	Aspirate	0	Load	
	(d) Cleaning	1000	25	In	Dispense	8	Load	
(2) Column conditioning	(a) 0.1 M acetate buffer	1500	200	In	Aspirate	6	Load	
	(b) Conditioning	1500	25	In	Dispense	8	Load	
(3) Sample loading	(a) Sample	2×3000	200	In	Aspirate	1	Load	
	(b) Loading	2×3000	25	In	Dispense	8	Load	
(4) Washing	(a) 0.1 M buffer	600	200	In	Aspirate	6	Load	
	(b) Washing	600	20	In	Dispense	8	Load	
(5) Bi plating	(a) 1 M HCl	150	200	In	Aspirate	4	Load	−1.3
	(b) Bi(III) plating solution	450	200	In	Aspirate	2	Load	
	(c) Plating	600	12	In	Dispense	7	Load	
(6) Eluting & deposition of metal	(a) 1 M HCl	720	200	In	Aspirate	4	Elute	−1.3
	(b) Eluting & deposition	720	12	In	Dispense	8	Elute	
	(c) Reversal flow of eluate	120	12	In	Aspirate	8	Elute	
	(d) Solution in (c)	120	12	In	Dispense	8	Elute	
(7) Equilibration	–	–	0		–	8		−1.3
(8) Stripping & recording	–	–	0		–	8		−1.2 to +0.3
(9) Electrode cleaning	(a) 1 M HCl	3000	200		Aspirate	4	Load	+0.3
	(b) Cleaning	3000	50		Dispense	7	Load	

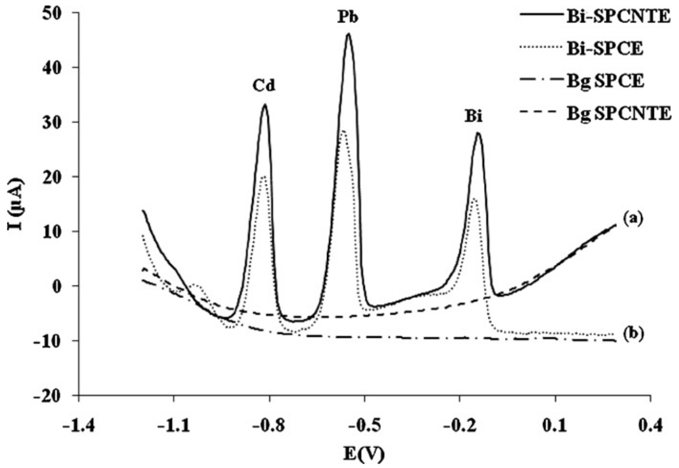

Fig. 2. Comparison of voltammograms of a solution containing $50\,\mu g\,L^{-1}$ Pb(II) and Cd(II) ions in 0.1 M acetate buffer (pH 4) at in situ plated (a) Bi-SPCNTE and (b) Bi-SPCE. Voltammograms of both electrodes are also shown as background current (Bg SPCNTE and Bg SPCE). Conditions: sample volume 3 mL, sample flow rate $20\,\mu L\,s^{-1}$, eluent volume 1.5 mL, eluent flow rate $12\,\mu L\,s^{-1}$, concentration of Bi(III) plating solution $150\,\mu g\,L^{-1}$, deposition potential −1.4 V, pulse amplitude 0.050 V, step potential 0.005 V, frequency 50 Hz.

The sample volume has a direct effect on the sensitivity of this method, where, typically, for a given sample analyte concentration, a large sample volume can increase the amount of adsorbed analyte in SPE and improve the detection sensitivity. However, the maximum sample volume that can pass through the SPE column is limited by the sorbent capacity. Therefore, a breakthrough volume was evaluated for $50\,\mu\,L^{-1}$ Pb(II) and Cd(II) ion sample solutions within a 3–50 mL range. The ASV signals were found in the sample after passing through the mini-column when the sample volume was higher than 12 mL for Pb(II) and 6 mL for Cd(II). Presumably the excess sample loading volume provided an excess amount of metal ions over the sorbent binding capacity. Hence, the optimum loading volume was chosen as 6 mL for subsequent assays at these Pb(II) and Cd(II) concentrations for high sensitivity without overloading the sorbent capacity.

The washing step is then required to remove the coadsorbed matrix materials from the SPE column, and for this water and 0.1 M acetate buffer (pH 3) were evaluated as washing solutions by performing step sequences from 1 to 9 (Table 1). The ASV signals after washing with acetate buffer was higher than that obtained after washing with water, and thus 0.1 M acetate buffer (pH 3) was used as the washing solution from hereon in this work.

For the elution step, 1 M HCl was used to remove all of the adsorbed analytes from the chelating resin column. This eluent was also used as a supporting electrolyte for the ASV detection. With increasing HCl concentration, the hydrogen evolution at the electrode surface was increased and the current signals of Pb(II) and Cd(II) were decreased. Therefore, HCl at higher concentration than 1 M was not suitable for this work. To study the performance of the elution step, steps 6–9 (Table 1) were repeated after the electrode cleaning step (step 9), but no analyte peaks were detected in the eluate obtained by repeated elution, suggesting the complete elution of the analytes in the first elution.

3.3. *Effect of the sample pH*

Factors affecting the collection and elution of Pb(II) and Cd(II) ions on the Analig TE-05 chelating resin mini-column were studied. The sample pH has a direct effect on the ability of the mini-column to bind Pb(II) and Cd(II) ions from the sample solution. Therefore, the influence of the sample pH on the square-wave ASV signals of Pb(II) and Cd(II) was evaluated from pH 2 to 7 by adjusting the pH of metal ions solution with 0.1 M acetate buffer. The peak current of Pb(II) was maximal in the range of pH 2–4 and thereafter decreased at pH 5 and reached a minimal level at pH 6 and 7. However, Cd(II) showed two peaks, a slight maximum at pH 3 and then a highest peak at pH 7. As a compromise, the efficient collection of both metals at the same time could be attained at a sample pH of 3.

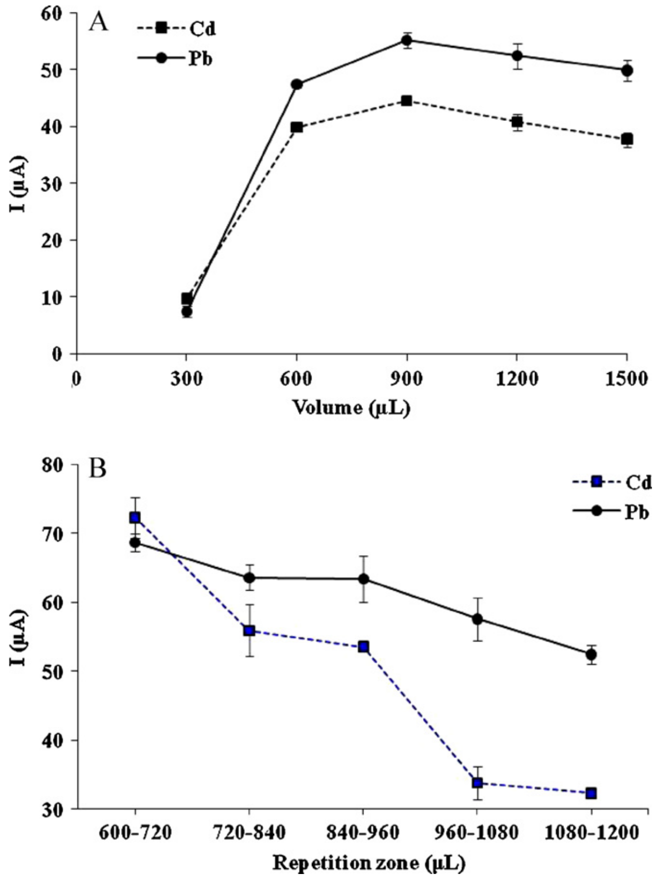

Fig. 3. Effect of (A) eluent volume and (B) repeated deposition of various eluate zones (fractions) on the ASV peak currents of a solution containing $50\,\mu g\,L^{-1}$ Pb(II) and Cd(II) ions in 0.1 M acetate buffer (pH 3) after preconcentration on an Analig TE-05 resin mini-column and eluting with 1 M HCl. Conditions are the same as in Fig. 2. Data are shown as the mean±SD and are derived from three replicates.

3.4. *Effect of eluent volume*

The effect of eluent (1 M HCl) volume on the ASV peak currents for Pb(II) and Cd(II) ion containing samples was investigated in the range of 300–1,500 μL, where the eluent volume of 600 μL was sufficient for complete elution of Pb(II) and Cd(II) from the mini-column. However, the eluent volume in the range of 600–1,200 μL was found to give the highest analytical signal (Fig. 3A) because larger volume of eluent was required to pass through the PTFE tubing of SIA system before it reached the electrochemical flow cell. Therefore, this eluent volume range was selected for further evaluation as detailed below.

Typically, each eluate zone has a different concentration of metal ions. In order to increase the sensitivity, the metal ion-rich zone of eluate should be allowed to flow backwards and forwards over the working electrode during the deposition step, as repeating the deposition of the metal should increase the deposition time. Thus, the effect of repeated deposition on the stripping peak currents was evaluated for 120 μL portions of the eluate from 600 to 1,200 μL, by aspirating the selected 120 μL zone backwards and forwards

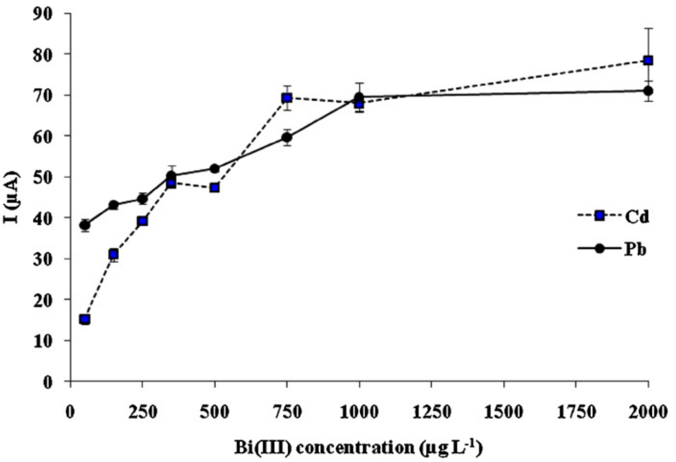

Fig. 4. Effect of the concentration of the Bi(III) plating solution on the ASV peak currents of a solution containing 50 μg L^{-1} Pb(II) and Cd(II) in 0.1 M acetate buffer (pH 3) after preconcentration on an Analig TE-05 resin mini-column and eluting with 1 M HCl. Conditions are the same as in Fig. 2, except eluate zone of repeated deposition 600–720 μL. Data are shown as the mean±SD and are derived from three replicates.

through the flow cell. The highest ASV peak currents of Pb(II) and Cd(II) were both obtained when the deposition stage was repeated with the metal ion-rich eluate zone of 600–720 μL (Fig. 3B), and so repeated deposition of this eluate portion was chosen for subsequent analysis to obtain a higher sensitivity.

3.5. *Effect of the Bi(III) concentration*

For the working electrode, a Bi film was produced on SPCNTEs by on-line in situ plating. The thickness of the Bi film, which depends on the Bi(III) ion concentration, will affect the voltammograms obtained. Thus, the effect of the concentration of the Bi(III) plating solution on the obtained ASV peak currents of Pb(II) and Cd(II) was investigated over the concentration range of 50–2,000 μg L^{-1}. As the Bi(III) concentration increased up to 1,000 μg L^{-1}, the ASV peak currents of Pb(II) and Cd(II) also increased, and then as the Bi(III) concentrations increased further the signal remained at the same level for Pb(II) but increased slightly for Cd(II), but with a larger variation of data (Fig. 4). Moreover, the SPCNTEs were difficult to clean at Bi(III) concentrations higher than 1,000 μg L^{-1}. Therefore, the suitable Bi(III) concentration was chosen to be 1,000 μg^{-1}.

3.6. *Effect of the deposition potential*

The influence of the deposition potential on the obtained stripping peak currents of Pb(II) and Cd(II) was examined at −1.0 to −1.5 V vs. Ag/AgCl, and a deposition potential of −1.3 V vs. Ag/AgCl was found to be optimal, as it gave the highest stripping peak currents.

3.7. *Effect of square-wave voltammetric parameters*

The effect of the square-wave frequency, step potential and amplitude on the obtained ASV peak currents of Pb(II) and Cd(II) were also investigated. The peak currents of Pb(II) and Cd(II) increased as the square-wave frequency and step potential increased, but with peak broadening. The frequency and step potential define the effective scan rate. Hence, an increase in either the frequency or step height results in an increase in the effective scan rate. The optimum frequency and step potential were found to be 75 Hz and 4 mV, respectively, and were used for all subsequent measurements. An increase in the amplitude caused an increment in the peak currents for both Pb(II) and Cd(II), due to the larger difference between the cathodic and anodic currents, with the optimum square-wave potential amplitude being 50 mV.

Table 2
Optimized experimental conditions for the on-line preconcentration and determination of Pb(II) and Cd(II) ions using the SIA/ASV system.

Parameter	Range examined	Optimized value
Sample pH	2–7	3
Eluent volume	300–1,500 μL	720 μL
Eluate zone of repeated deposition	600–1,200 μL	600–720 μL
Eluent flow rate	4–15 μL s^{-1}	12 μL s^{-1}
Concentration of Bi(III) plating solution	50–2,000 μg L^{-1}	1,000 μg L^{-1}
Deposition potential	−1.0–−1.5 V	−1.3 V
Frequency	10–100 Hz	75 Hz
Step potential	1–5 mV	4 mV
Amplitude	10–60 mV	50 mV

3.8. *Effect of the eluent flow rate*

The influence of the flow rate of the 1 M HCl, as eluent, on the square-wave ASV signals of Pb(II) and Cd(II) was investigated in the range of 4 to 15 μL s^{-1}. The stripping peak currents of both metals were maximal at a flow rate of 6 μL s^{-1}, slightly higher than those obtained at the flow rate of 12 μL s^{-1}. However, a flow rate of 12 μL s^{-1} was chosen as the sensitivity is almost as high as that at 6 μL s^{-1} but the analysis time would be significantly shorter.

In order to evaluate the effective success of the preconcentration procedure, the determination of Pb(II) and Cd(II) ions in a solution containing 20 μg L^{-1} Pb(II) and Cd(II) were performed under the optimum experimental conditions (summarized in Table 2) with and without the mini-column preconcentration stage. The results showed that the ASV signal for both metal ions by SIA/ASV on Bi-SPCNTE was significantly improved (Fig. 5), with enrichment factors of 11.9-fold for Pb(II) and 6.6-fold for Cd(II) being obtained. The ASV method using Bi-SPCNTE was inherently 2.2-fold more sensitive to Cd(II) than Pb(II) for the process without the mini-column preconcentration but was conversed to 1.2-fold for the process with the mini-column preconcentration. This may be caused by the electrode surface saturation at higher metal ion concentration. For this reason, the enrichment factor for Cd(II) was much lower than that for Pb(II).

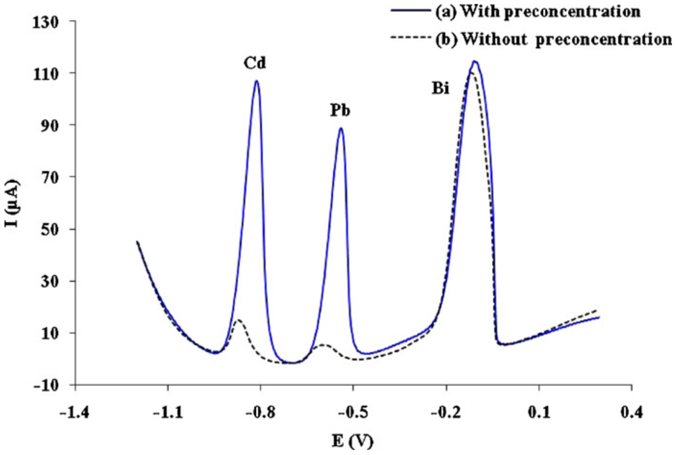

Fig. 5. Comparison of the voltammograms from the square-wave ASV of a solution containing 20 μg L^{-1} Pb(II) and Cd(II) ions in 0.1 M acetate buffer (pH 3) with a Bi-SPCNTE under the optimum conditions (a) with and (b) without preconcentration on a mini-column. Conditions: sample volume 6 mL, sample flow rate 25 μL s^{-1}, eluate zone of repeated deposition; 600–720 μL; eluent flow rate 12 μL s^{-1}, concentration of Bi(III) plating solution: 1000 μg L^{-1}; deposition potential: −1.3 V; pulse amplitude: 0.050 V, step potential: 0.004 V, frequency: 75 Hz. Data are shown as the mean±SD and are derived from three replicates.

3.9. *Effect of interference from other ions*

Although the mini-column of chelating resin, Analig TE-05, was used for preconcentration and separation of Pb(II) and Cd(II) ions for the determination by ASV, several metal ions can be adsorbed on the chelating resin and eluted from the mini-column into the electrochemical flow cell [17]. Moreover, if other ions are present in the sample at high concentration, they may attach the active sites and prevent Pb(II) and Cd(II) ions from being adsorbed [18]. Therefore, the effect of other ions in the sample as potential sources of interference during any part of on-line preconcentration and determination of Pb(II) and Cd(II) ions were investigated as the concentration ratio of the desired analyte (Pb(II) and Cd(II) ions) to the potential interference one. That is the analytical responses of a solution containing only Pb(II) and Cd(II) ions at 5 $\mu g\,L^{-1}$ was compared with the addition of the potential interfering ions at various concentration ratios. Interference was defined as when a negative or positive change of 10% or more was seen compared to the response recovery of the analyte alone [19]. A 1000-fold or higher excess of Fe^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, K^{+}, $SO_4{}^{2-}$, $NO_3{}^{-}$ and Cl^{-} ions each had no significant affect on the ASV signals of Pb(II) and Cd(II), and so do not interfere. A tolerated ratio of interference on the Pb(II) signal was seen at a 1000-fold excess of Co(II) and a one-fold excess of Cu(II), whereas a 10-fold excess of Zn(II) and a one-fold excess of Sb(III) had an interfering influence on the signal of both Pb(II) and Cd(II) analytes.

Co(II) ions cause a positive error on the ASV signal, with the current increase being due to the formation of a cobalt film on the SPCNTE [20], whilst Sb(III) and Zn(II) ions caused a reduction in the ASV signal and so underestimate the Pb(II) and Cd(II) ion levels. From the literature, higher Sb(III) concentrations will likely cause additional oxidation, due to the complexity of oxidation states of Sb(III) [21]. The same oxidation peaks were also observed in the absence of Pb(II) and Cd(II) ions. In the case of the Zn(II) ion interference, these ions also decrease the ASV current signal, the same trend as that seen for Sb(III), but the tolerated ratio of Zn(II) was 10-fold higher. The increasing ASV signal from Zn(II) ions is a problem since the relatively narrow oxidation potential range between Zn(II) and Cd(II) ions makes it difficult to resolve the correct response.

Cu(II) ions appear to be an important interfering ions. When the concentration of Cu(II) was increased, the ASV peak currents of Pb(II) and Cd(II) decreased. To improve the current signal and eliminate Cu(II) interference in ASV, Ga(III) ions are usually added to the supporting electrolyte and typically slightly improve the recovery of Pb(II) and Cd(II) [22].

3.10. *Analytical characteristics*

Calibration curves of the on-line preconcentration and determination of Pb(II) and Cd(II) ions were prepared under the optimum conditions (Table 2). The ASV peak currents of Pb(II) and Cd(II) had a linear relationship with the ion concentration in the range of 0.5–15 $\mu g\,L^{-1}$ and 15–70 $\mu g\,L^{-1}$, but with a different slope. The slope of the calibration curves between the stripping peak currents and the concentration were 4.96 $\mu A\,\mu g^{-1}\,L$ for Pb(II) and 6.97 $\mu A\,\mu g^{-1}\,L$ for Cd(II) over a linear range of 0.5–15 $\mu g\,L^{-1}$ and 0.82 $\mu A\,\mu g^{-1}\,L$ for Pb(II) and 0.80 $\mu A\,\mu g^{-1}\,L$ for Cd(II) over a linear range of 15–70 $\mu g\,L^{-1}$, which suggests the higher sensitivity of the proposed method in a concentration range of 0.5–15 $\mu g\,L^{-1}$. In addition, the calibration lines for higher concentration range do not pass through the origin, which was probably caused by the electrode surface saturation at higher metal ion concentration leading to the deposition of Pb and Cd on the Pb–Cd film instead of the Bi film; thus, lower sensitivity for the determination of Pb(II) and Cd(II) were obtained. The relative standard deviations for 10 repeat measurements at three different concentrations were in the range of 2.56 to 5.67%. The limit of detection (LOD) was obtained at the concentrations as low as 0.01 $\mu g\,L^{-1}$ for both metal ions. The limit of quantification (LOQ) was 0.50 $\mu g\,L^{-1}$ for Pb(II) and Cd(II). The total time per one analysis cycle was approximately 11 min. The LOD of this proposed method is much lower than that previously reported at 0.2 $\mu g\,L^{-1}$ for Pb(II) and 0.8 $\mu g\,L^{-1}$ for Cd(II) [13].

Table 3
Determination of the Pb(II) and Cd(II) ion concentrations in various water and food samples.

Samples	Spiked level ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)		Recovery (%)	
		Pb	Cd	Pb	Cd
Drinking water	0.00	ND	ND		
	4.00	4.29±0.55	4.54±0.36	107.2	113.6
	12.00	11.88±0.26	12.01±1.77	99.0	100.1
Pond water	0.00	ND	ND		
	4.00	3.79±0.25	3.29±1.91	94.7	82.1
	12.00	12.05±1.33	11.38±1.88	100.4	94.8
Tap water	0.00	1.69±0.15	ND		
	4.00	4.39±0.51	3.81±0.60	105.6	95.2
	12.00	11.33±1.29	11.62±1.85	93.0	96.9
Green tea	0.00	ND	ND		
	4.00	3.22±1.01	2.50±1.59	80.4	62.5
	12.00	8.21±0.45	7.26±0.25	68.4	60.5
Soup	0.00	2.06±0.10	ND		
	4.00	3.47±0.35	4.14±0.62	81.6	103.5
	12.00	9.94±1.00	9.65±0.92	81.1	80.4
Fish	0.00	ND	ND		
	4.00	4.29±1.06	4.61±0.61	107.3	115.3
	12.00	12.16±0.89	12.09±0.40	101.3	100.8
Cockle	0.00	ND	ND		
	4.00	4.53±1.00	4.73±0.66	108.2	118.2
	12.00	11.54±1.10	10.98±1.07	94.4	91.5

ND=not detected.

3.11. *Application in water and food samples*

The on-line preconcentration method in this present work was then evaluated the determination of trace amounts of Pb(II) and Cd(II) ions in drinking water, pond water, tap water, green tea, soup, fish and cockles. Each sample type was divided into three portions and spiked with 0, 4 or 12 $\mu g\,L^{-1}$ of both Pb(II) and Cd(II), respectively. The samples were then diluted into the low concentration linear range (0.5–15 $\mu g\,L^{-1}$) and evaluated. The analytical results obtained are summarized in Table 3. The recovery efficiencies of both metal ions were obtained in the range of 60.5–118.2%, which are acceptable under all conditions.

In addition, the method of this report was compared with the standard ICP-OES method on the same samples for direct comparison, except that the sample dilution was performed to be within the high concentration linear range (15–70 $\mu g\,L^{-1}$) for Pb(II) and Cd(II) because the ICP-OES method cannot detect low concentrations of Pb(II) or Cd(II) ions. The comparison between the proposed method of this study and ICP-OES was performed on the noodle soup, fish, cockle and green tea samples since they have a higher matrix interference than the water samples. No significant difference between the two methods was found, which suggests that this proposed method is reliable and acceptable under all conditions, as well as more sensitive.

4. Conclusions

An automated sequential injection method for the on-line pretreatment and simultaneous determination of Pb(II) and Cd(II) ion concentrations using a SPE on the Analig TE-05 resin mini-column in conjunction with ASV at the Bi-SPCNTE was developed for the first time. Enrichment factors of 11.9-fold and 6.6-fold for Pb(II) and Cd(II) ions, respectively, were obtained by the on-line preconcentration of analytes on the SPE mini-column. The proposed method provides a cost-efficient, environmental-friendly, convenient and highly sensitive quantification of ultra-trace Pb(II) and Cd(II) ion concentrations.

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