

On-line Preconcentration and Determination of Trace Heavy Metals by Sequential Injection-Anodic Stripping Voltammetry Using Bismuth Film Screen-printed Carbon Electrode

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Abstract

An automated on-line preconcentration method was developed for simultaneous determination of Pb(II), Cd(II) and Zn(II) by square-wave anodic stripping voltammetry (SWASV) using bismuth film screen-printed carbon electrode (Bi-SPCE). The preconcentration of metal ions was performed with a mini-column of a chelating resin, which was installed on a switching valve in the automated system consisted of a syringe pump, an 8-port selection valve and a switching valve. The laboratory-assembled automated on-line pretreatment system (Auto-Pret ASV system) was controlled by the Visual Basic program written by the authors. The metal ions collected on the resin were eluted with 1 M hydrochloric acid, subsequently transported into the flow cell for on-line deposition of analytes on Bi-SPCE at -1.4 V vs. Ag/AgCl; then the flow of the solution was stopped and the voltammogram was recorded from -1.2 to 0.2 V vs. Ag/AgCl by scanning a potential in the square-wave waveform. Experimental conditions, such as pH of sample, a sample flow rate, an eluent volume and its flow rate were optimized. Under the optimum conditions, the analytical characteristics were studied. In addition, the proposed method was applied to the analysis of water samples.

Keywords On-line preconcentration, sequential injection, heavy metals, anodic stripping voltammetry, bismuth film screen-printed carbon electrode

1. Introduction

The determination of heavy metals in natural waters, drinking waters and foods is essential and important for human health and safety. Heavy metal contents in such samples are usually found at trace levels, thus, the analytical methods of high selectivity and lower detection limit are required.

Anodic stripping voltammetry (ASV) is recognized as one of the most powerful tools in trace and ultratrace analysis of metal ions because it provides wide linear dynamic range, low detection limit, and multi-element analysis capability. The high sensitivity and selectivity of ASV is attributed to the deposition step in which the analytes are cathodically preconcentrated onto the working electrode before the stripping detection of the accumulated metals. An additional advantage of ASV over flame atomic absorption spectrophotometry (FAAS), electrothermal atomic absorption spectrophotometry (ETAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS), is the simplicity of the instrumentation, which is relatively inexpensive, requires low electrical power and low maintenance, and is portable as well as suitable for automation [1-3].

Combining stripping voltammetry with flow systems has significant advantages over batch analysis, such as high level of automation, speed of analysis, improvement of accuracy and precision, less risk of contamination and cost-effective operation [4-5]. Sequential injection analysis (SIA) is the flow analysis techniques suited to stripping techniques [6]. SIA allows ASV to be performed with high precision because of the excellent reproducibility of time and mixing conditions, leading to very reproducible mass transport between the electrode surface and

the flowing stream solution [7]. Various stripping voltammetric methods which were automated by SIA have been reported [4-10].

In many cases, however, the concentration of analyte metals in water samples is extremely low. Besides the electrochemical preconcentration of analytes on the surface of electrode, an appropriate sample preconcentration must be included in an analytical method to increase the detection sensitivity. The methods which are based on sorbent extraction have proven to be the most attractive ones due to their high preconcentration efficiency. This method allows also efficient elimination of some matrix effects. Moreover, they can be easily implemented and controlled in the flow systems [11]. SIA is currently viewed as a powerful analytical technique for automated sample pretreatment and trace-level assay [12]. Several sequential injection on-line pretreatment for the determination of trace metals by spectrophotometry, FAAS, ETAAS, ICP-AES and ICP-MS have been reported. However, they have not been used for the determination of metals by ASV [13-15].

In this work, an automated sample pretreatment and anodic stripping voltammetric determination system (Auto-Pret ASV system) for simultaneous determination of Pb(II), Cd(II) and Zn(II) by square-wave anodic stripping voltammetry (SWASV) using environmentally friendly electrode, bismuth film screen-printed carbon electrode (Bi-SPCE), has been developed.

2. Experimental

2.1 Reagents

All standard and reagent solutions were prepared with ultrapure and analytical grade reagents using ultrapure water (resistivity $\geq 18.3 \text{ M}\Omega \text{ cm}^{-1}$) from Milli-Q Ultrapure Water Purification Systems (Millipore, USA). The working standard

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solutions of Pb(II), Cd(II) and Zn(II) were daily prepared by appropriate dilution of the stock standard solutions (1000 mg L⁻¹ atomic absorption analysis standard solution, BDH Chemicals, England) with 1 M hydrochloric acid solution. A 500 µg L⁻¹ Bi(III) plating solution was prepared by appropriate dilution of the stock solution of Bi (1000 mg L⁻¹ atomic absorption analysis standard solution, Wako Pure Chemical Industries, Japan) with 1 M hydrochloric acid solution. A 1 M hydrochloric acid solution, served as an eluent as well as a supporting electrolyte, was prepared by appropriate dilution of hydrochloric acid (analytical grade, 37%, 1.19 g mL⁻¹, Merck KGaA, Germany). A 0.1 M acetate buffer solution was prepared by dissolving 13.6 g of sodium acetate trihydrate (analytical grade, Merck, Germany) in 800 mL of ultrapure water, adding appropriate volume of glacial acetic acid (analytical grade, 99.9%, 1.05 g mL⁻¹, Carlo Erba, Germany) and diluting to 1000 mL with ultrapure water. The chelating resin, ME-1 (GL Sciences, Japan), was packed in a PTFE tubing (2 mm i.d. and 4.5 cm length) equipped with the plugs of glass wool at both ends to entrap the resin in the mini-column. The water samples were adjusted to pH 4 just before introduced to the sequential injection system.

2.2 Apparatus

A laboratory-assembled sequential injection for pretreatment and anodic stripping voltammetric determination system, Auto-Pret ASV system, as shown in Figure 1, consisted of a 3-way syringe pump (Hamilton, USA), an 8-port selection valve (Hamilton, USA) and a 6-port switching valve (Hamilton, USA). A mini-column of a chelating resin was installed on a switching valve. PTFE tubing was used for flow lines (0.5 mm i.d.) and a holding coil (1.5 mm i.d.). Electrochemical measurements were carried out in a thin-layer flow cell (Bioanalytical Systems, USA) using Autolab PGSTAT 100 Potentiostat (Eco Chemie, The Netherlands). The pump and valves were computer controlled by using a program written by Visual Basic software.

The thin-layer flow cell consisted of a gasket as a spacer, a screen-printed electrode (SPCE) as a working electrode, a Ag/AgCl (3 M KCl) electrode as a reference electrode, and a stainless steel tube as a counter electrode as well as a solution outlet of the flow cell. The electrodes were screen-printed in house using carbon ink (Electrodag PF-407C, Acheson, USA), silver ink (Electrodag 7019, Acheson, USA) on ceramic substrates. Bismuth film screen-printed carbon electrodes (Bi-SPCE) were prepared by on-line *in situ* plating. The ASV experiments were carried out in a Faraday cage to reduce electrical noise. Hydrochloric acid, 1 M, was used as a supporting electrolyte. All experiments were performed at room temperature (25°C) without removing oxygen from the solution.

2.3 Operating procedures

Step sequence for on-line preconcentration and determination of Pb(II), Cd(II) and Zn(II) using Auto-Pret ASV system are shown in Table 1. First, the switching valve was set to the loading stage, as shown in Figure 1. One milliliter of 2 M hydrochloric acid was aspirated via the selection valve into the holding coil, and then dispensed in reverse direction through the mini-column, followed by flowing 1 mL of ultrapure water for cleaning the column (step 1). Second, 1.5 mL of a 0.1 M acetate buffer was aspirated and dispensed into the mini-column for column conditioning (step 2). Third, 3 mL of a sample solution, the pH of which was adjusted to appropriate pH, was aspirated and introduced into the mini-column (step 3) for preconcentration and separation of matrices. This sample loading step was repeated two times to introduced total sample volume.

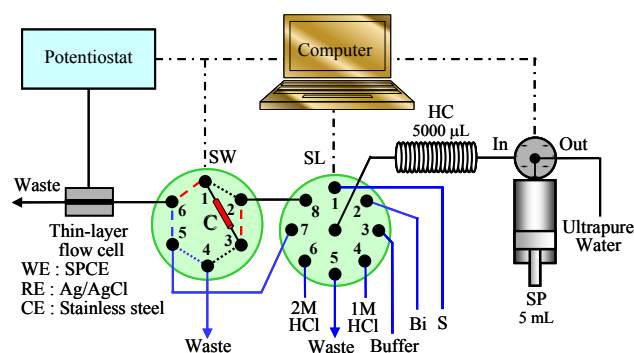


Fig. 1 Schematic diagram of sequential injection for pretreatment and anodic stripping voltammetric determination system, Auto-Pret ASV system, for on-line preconcentration and determination of Pb(II), Cd(II) and Zn(II). SP: syringe pump; SL: selection valve; SW: switching valve (····· loading stage, --- eluting stage); HC: holding coil; C: minicolumn (2 mm i.d. and 4.5 cm length); S: sample/standard solution; Bi: Bismuth(III) plating solution; Buffer: 0.1 M acetate buffer; 1 M HCl: electrode cleaning solution; 2 M HCl: column cleaning solution; WE: working electrode; RE: reference electrode; CE: counter electrode.

of 6 mL. Fourth, 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 deposited on the electrode at -1.4 V vs. Ag/AgCl to form Bi film on SPCE (step 4). After the switching valve was turned to the eluting stage, 0.7 mL of 1 M hydrochloric acid was aspirated and dispensed to elute collected metal ions in the mini-column. When the eluate flowed into the thin-layer flow cell, the metal ions were deposited on Bi-SPCE at -1.4 V vs. Ag/AgCl. In order to increase the sensitivity, 0.1 mL of the eluate concentrated with analyte metal ions was aspirated in reversed direction and dispensed into the thin-layer flow cell again (step 5). Then the flow of the solution was stopped, after 10 s equilibration time (step 6) the voltammogram was recorded from -1.2 to 0.2 V vs. Ag/AgCl by scanning a potential in the square-wave waveform with a frequency of 50 Hz, a step potential of 4 mV, and a pulse amplitude of 40 mV (step 7). Finally, the switching valve was set to the loading stage, 1.5 mL of 1 M hydrochloric acid was aspirated and dispensed into the thin-layer flow cell in which the SPCE was cleaned from remaining analyte metals and Bi film at +0.3 V vs. Ag/AgCl (step 8).

3. Results and Discussion

3.1 Optimization of the on-line preconcentration procedures

Factors affecting the collection and elution of Pb(II), Cd(II) and Zn(II) on the mini-column were studied.

The effect of sample pH on the square wave anodic stripping voltammetric signals of Pb(II), Cd(II) and Zn(II) was examined in the range of pH 2 to 7 by adjusting the pH of metal ion solution with hydrochloric acid or 0.1 M acetate buffer solution. For further experiment, the sample pH of 4 was selected for the preconcentration and simultaneous determination of Pb(II), Cd(II) and Zn(II) with high sensitivity and good reproducibility (small error bars).

The sample loading flow rate did not give any significant effect on analytical signals. A flow rate of 25 µL s⁻¹ was employed to achieve a sorption equilibrium of metal ions on the resin and avoid high pressure of the mini-column.

Table 1 Step sequence for the on-line preconcentration and determination of metal ions using Auto-Pret ASV system

Step	Operating description	Volume / μL	Flow rate / $\mu\text{L s}^{-1}$	Syringe valve position	Syringe pump status	Valve position		Electrode Potential / V vs. Ag/AgCl
						SL	SW	
1) Column cleaning	a) 2 M HCl	1000	200	In	Aspirate	6	Load	-1.0 (Conditioning potential)
	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 buffer	1500	200	In	Aspirate	3	Load	-1.0
	b) Conditioning	1500	25	In	Dispense	8	Load	
3) Sample loading	a) Sample	2×3000	200	In	Aspirate	1	Load	-1.0
	b) Loading	2×3000	25	In	Dispense	8	Load	
4) Bi plating	a) Bi(III) plating solution	600	200	In	Aspirate	2	Load	-1.0 -1.4
	b) Plating	600	10	In	Dispense	7	Load	
5) Eluting & deposition of metal	a) 1 M HCl	700	200	In	Aspirate	4	Elute	-1.4
	b) Eluting & deposition	400	10	In	Dispense	8	Elute	
	c) Reversal flow of eluate	100	10	In	Aspirate	8	Elute	
	d) Solution in c) and 1 M HCl	100 + 300	10	In	Dispense	8	Elute	
6) Equilibration	-	-	0 (10 s)	-	-	8	Elute	-1.4
7) Stripping & recording	-	-	0	-	-	8	Elute	Scan (-1.2 to -0.2)
8) Electrode cleaning	a) 1 M HCl	1500	200	-	Aspirate	4	Load	+0.3
	b) Cleaning	1500	50	-	Dispense	7	Load	

A solution of 1 M hydrochloric acid was used as an eluent because it was an excellent supporting electrolyte for detection of Pb(II), Cd(II) and Zn(II) by SWASV with high sensitivity and without damaging of SPCE [10].

The influence of the flow rate of 1 M hydrochloric acid, as eluent, on the square wave anodic stripping voltammetric signals of Pb(II), Cd(II) and Zn(II) was studied in the range of 4 to 12 $\mu\text{L s}^{-1}$. It was observed that the stripping peak currents of all metals were slightly affected by the flow rate of eluent. However, large error bars were obtained at slow flow rate for the reason that hydrogen gas was generated at the surface of working electrode in the deposition step and shielded the electrode from the solution. Therefore, the flow rate of 10 $\mu\text{L s}^{-1}$ was chosen for good reproducibility (small error bar) and short analysis time.

The effect of the volume of eluent, 1 M hydrochloric acid, on the anodic stripping peak currents of Pb(II), Cd(II) and Zn(II) was investigated in the range of 400 to 1200 μL . The results showed that there is no significant increase in stripping peak currents when 1 M hydrochloric acid was increased above 700 μL . Therefore, 700 μL of 1 M hydrochloric acid was used for complete elution of metal ions from the mini-column.

For the determination of metal ions by ASV, enhancement of sensitivity can be achieved through increasing the deposition periods. In this work, the deposition time was increased by passing back and forth of the metal ion-rich zone of eluate over the working electrode in the thin-layer flow cell during the deposition step for repeated deposition. The effect of repeated deposition of various zone of eluate on the stripping peak currents were studied in the range of 100 to 600 μL by aspirating of 100 μL each backward and forward through the flow cell. The results in Figure 2 show that the highest stripping peak currents of Pb, Cd and Zn were obtained when repeated deposition of eluate in the zone of 300-400 μL was carried out by aspirating this zone through the flow cell in the reversed direction and dispensed through the flow cell again. Therefore, this procedure was used for higher sensitivity.

The optimized conditions are summarized in Table 2.

In order to evaluate the effectiveness of the preconcentration procedure, the determination of Pb(II), Cd(II) and Zn(II) in

Table 2 Optimization of experimental conditions for on-line preconcentration using Auto-Pret ASV system

Parameter	Range examined	Optimized value
Sample pH	2 to 7	4
Eluent flow rate	2 to 14 $\mu\text{L s}^{-1}$	10 $\mu\text{L s}^{-1}$
Eluent volume	400 to 1200 μL	700 μL
Zone of repeated deposition	100 to 600 μL (100 μL each)	300 to 400 μL

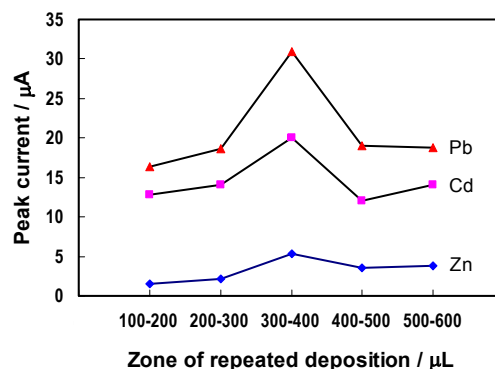


Fig. 2 Effect of repeated deposition of various zone of eluate on the stripping peak currents of a solution containing 10 $\mu\text{g L}^{-1}$ Pb(II), 10 $\mu\text{g L}^{-1}$ Cd(II) and 50 $\mu\text{g L}^{-1}$ Zn(II) in 0.1 M acetate buffer (pH 4) after preconcentration on a mini-column and eluting with 1 M hydrochloric acid. Conditions: sample volume: 6 mL, sample flow rate: 25 $\mu\text{L s}^{-1}$; eluent volume: 700 μL ; eluent flow rate 10 $\mu\text{L s}^{-1}$, concentration of Bi(III) plating solution: 500 $\mu\text{g L}^{-1}$; conditioning potential: -1.0 V; deposition potential: -1.4 V; equilibration time: 10 s; pulse amplitude: 0.040 V; step potential: 0.004 V; frequency: 50 Hz.

solutions containing 50 $\mu\text{g L}^{-1}$ Pb(II), 50 $\mu\text{g L}^{-1}$ Cd(II) and 150 $\mu\text{g L}^{-1}$ Zn(II) were performed under the optimum experimental conditions with and without the mini-column. The results showed that the sensitivity for the determination of all metal ions by SWASV on Bi-SPCE was significantly improved.

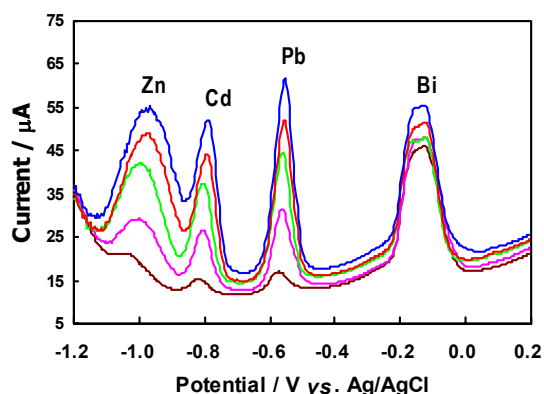


Fig. 3 Square-wave anodic stripping voltammograms on Bi-SPCE of the solutions containing Pb(II), Cd(II) and Zn(II) of increasing concentrations: 2, 6, 10, 12 and 14 $\mu\text{g L}^{-1}$ for Pb(II) and Cd(II); and 20, 30, 40, 50 and 70 $\mu\text{g L}^{-1}$ for Zn(II). Conditions: sample volume: 6 mL, sample flow rate: 25 $\mu\text{L s}^{-1}$; eluent volume: 700 μL ; eluent flow rate 10 $\mu\text{L s}^{-1}$, zone of repeated deposition 300-400 μL ; concentration of Bi(III) plating solution: 500 $\mu\text{g L}^{-1}$; conditioning potential: -1.0 V; deposition potential: -1.4 V; equilibration time: 10 s; pulse amplitude: 0.040 V, step potential: 0.004 V, frequency: 50 Hz.

3.2 Analytical characteristics

A calibration plot of the proposed method for the on-line preconcentration and simultaneous determination of Pb(II), Cd(II) and Zn(II) was prepared under the optimum conditions. Typical square-wave anodic stripping voltammograms on Bi-SPCE of the solutions containing Pb(II), Cd(II) and Zn(II) of various concentrations are shown in Figure 3. The stripping peak current has a linear relationship with the concentration in the range of 0–14 $\mu\text{g L}^{-1}$ for Pb(II) ($R^2 = 0.9972$), 0–14 $\mu\text{g L}^{-1}$ for Cd(II) ($R^2 = 0.9966$), and 20–50 $\mu\text{g L}^{-1}$ for Zn(II) ($R^2 = 0.9985$). The slope of the calibration graph between the stripping peak current and the concentration over linear range, are 3.13 $\mu\text{A}/\mu\text{g L}^{-1}$ for Pb(II), 1.93 $\mu\text{A}/\mu\text{g L}^{-1}$ for Cd(II), and 0.70 $\mu\text{A}/\mu\text{g L}^{-1}$ for Zn(II), which suggests the high sensitivity of the proposed method. The lowest detectable concentrations were obtained at the concentrations as low as 0.05 $\mu\text{g L}^{-1}$ for Pb(II), 0.3 $\mu\text{g L}^{-1}$ for Cd(II) and 17 $\mu\text{g L}^{-1}$ for Zn(II).

3.3 Analytical applications

The proposed method was applied to the determination of Pb(II), Cd(II) and Zn(II) in a bottled drinking water under the optimum conditions by the standard addition method. The results are shown in Table 3. The recoveries of Pb(II), Cd(II) and Zn(II) were in the range of 94.9–105%. The results obtained show that the proposed method can be successfully applied to the simultaneous determination of Pb(II), Cd(II) and Zn(II) in water samples.

4. Conclusion

An automated sequential injection for on-line pretreatment and anodic stripping voltammetric determination system, Auto-Pret ASV system, was for the first time developed for the simultaneous determination of Pb(II), Cd(II) and Zn(II) by SWASV using Bi-SPCE with high sensitivity. The proposed method were successfully applied to the determination of Pb(II), Cd(II) and Zn(II) in water samples.

Table 3 Results of Pb(II), Cd(II) and Zn(II) determination in drinking water sample by standard addition method.

Metal ion	Concentration / $\mu\text{g L}^{-1}$		Recovery / %
	Added	Found	
Pb(II)	0	ND	-
	2	1.9	95.2
	6	5.8	96.8
	8	8.3	104
	10	9.8	98.0
Cd(II)	0	ND	-
	2	2.0	100
	6	6.3	105
	8	8.4	105
	10	9.5	94.9
Zn(II)	0	ND	-
	20	20.1	101
	30	29.2	97.3
	35	36.1	103
	40	39.6	99.0

ND = not detected

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