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–$70\,\mu g\,L^{-1}$).

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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

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 ≥ 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$_2$SO$_4$: 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