



Determination of lead and cadmium in rice samples by sequential injection/ anodic stripping voltammetry using a bismuth film/crown ether/Nafion modified screen-printed carbon electrode

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ABSTRACT

A highly sensitive automated method for the determination of Pb^{2+} and Cd^{2+} by sequential injection/ anodic stripping voltammetry using a crown ether/Nafion modified screen-printed carbon electrode coated with a bismuth film was developed. The bismuth film was prepared by *in situ* depositing of Bi^{3+} simultaneously with the analyte metal ions on the modified electrode at -1.2 V vs. Ag/AgCl reference electrode for 180 s, using hydrochloric acid as a supporting electrolyte. Under the optimal conditions, estimated from sequential univariate analysis of each of the parameters, a linear detection range of 0.5 – 60 $\mu g\ dm^{-3}$ for both metal ions was found, with a LOD ($3S_b/S$) of 0.11 $\mu g\ dm^{-3}$ for Pb^{2+} and 0.27 $\mu g\ dm^{-3}$ for Cd^{2+} . This method shows good reproducibility and stability and was successfully applied to measure Pb^{2+} and Cd^{2+} levels in rice and rice product samples, with good agreement with those obtained by the standard ICP-OES method.

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1. Introduction

Rice is an important food for humans across the world and the staple diet of many populations in the tropics. However, heavy metal contamination in rice from the environment is a critical issue for consumer's health and safety. Thus, the measurement of trace elements within rice or rice products in order to detect the quantity of each toxic element in rice is important. Lead (Pb) and cadmium (Cd) are two of the most toxic heavy metals to humans, and can easily be adsorbed from contaminated soil. Several analytical techniques, such as atomic absorption spectrometry (AAS) (Da-Col, Domene, & Pereira-Filho, 2009; Narin, Soyak, Elci, & Dogan, 2000; Soyak, Elci, & Dogan, 1999; Soyak, Karatepe, Elci, & Dogan, 2003; Soyak, Narin, & Dogan, 1997), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Sen, Shandil, & Shrivastava,

2011), ICP-mass spectrometry (Lachas et al., 1999; Schramel, Wendler, & Angerer, 1997). Although these techniques provide good sensitivity, they involve high instrument cost and large equipments. Recently, anodic stripping voltammetry (ASV) (Kubiak & Wang, 1989) have been widely used for the determination of heavy metals due to its relatively low cost, small and portable equipments. Moreover, ASV has been developed into one of the more highly sensitive methods for trace heavy metal ion detection as there is a contribution to the sensitivity from both the pre-concentration step and the measurement procedure (Florence, 1984; Kubiak & Wang, 1989; Wang, 1990). Therefore, ASV has been established as a powerful technique for heavy metal ion detection. To improve the accuracy, precision and speed of analysis, and to reduce the risk of contamination and provide a cost-effective operation, an automated online system is required. Various stripping voltammetric methods which are automated by the use of a sequential injection analysis (SIA) system have previously been reported for heavy metal analyses (Christian, 1994; Da Silva & Masini, 2000; Economou, 2005; Ivaska & Kubiak, 1997; Suteerapataranon, Jakmunee, Vaneesorn, & Grudpan, 2002). Mercury-based electrodes, such as mercury film electrodes and hanging mercury drop electrodes have been widely used as

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a traditional electrode for ASV. However, the well-known toxicity of mercury and the associated difficulties in handling and storage of mercury limits its use as an electrode material, leading to the development of mercury-free electrodes. The bismuth (Bi) film electrode was introduced as an alternative more environmental friendly electrode because it offers high sensitivity, well-defined peaks and highly reproducible stripping signals (Chuanwatanakul, Dungchai, Chailapakul, & Motomizu, 2008; Kefala & Economou, 2006; Rehacek, Hotovy, Vojs, & Mika, 2008; Svancara et al., 2006; Wang, Lu, Hocevar, Farias, & Ogorevc, 2000; Wang, Lu, Kirgoz, Hocevar, & Ogorevc, 2001). Furthermore, it is insensitive to dissolved oxygen and so the time-consuming deoxygenation step is eliminated. Previously the Bi film was typically plated onto a glassy carbon electrode (GCE) (Charalambous & Economou, 2005). However, the GCE surface required polishing quite frequently making the use of such electrodes for high precision online analysis with automated systems including SIA quite difficult. Many researchers have reported using a screen-printed carbon electrode (SPCE) (Chuanwatanakul et al., 2008; Injang et al., 2010) as a substrate for the Bi film electrode because it is inexpensive, disposable, flexible in design and easy to produce.

In the past few years, the development of modifications to SPCEs with various compounds has progressed. This has been performed by incorporating these modifiers into the carbon ink prior to the screen-printing step or by drop coating the modifying reagents onto the transducer surface. These can enhance the analytical sensitivity and selectivity of the electrodes by preconcentrating analytes onto the electrode surface in the accumulation step. Several modifiers have been used in the construction of SPCEs, but the selection of modifiers is determined by its application. Nafion, a perfluorosulfonate cation exchange polymer, is one of the most extensively employed agents as a modifier (Crowley & Cassidy, 2002; Gouveia-Caridade, Pauliukaite, & Brett, 2006; Kefala & Economou, 2006; Kefala, Economou, & Voulgaropoulos, 2004). The cation-exchange property of Nafion can be used to preconcentrate the cation and for excluding anionic interferences. In addition, the advantages associated with the use of Nafion coated electrodes are an improvement in terms of robustness toward mechanical damage. Alternatively, crown ethers are another excellent choice as a modifier in order to improve the efficiency of the electrode surface for metal ion detection because the specific metal cations can form complexes by fitting into the defined cavity of the appropriately selected crown structure (Gupta & Kumar, 1999).

The aim of this work was to combine the cation exchange property of Nafion with the selective complexing ability of a crown ether, in this case dibenzo-24-crown-8 (D24C8), to fabricate a highly sensitive *in situ* plated Bi film D24C8/Nafion modified SPCE (Bi-D24C8/Nafion SPCE) for the simultaneous quantification of trace Pb^{2+} and Cd^{2+} by automated SIA–ASV. It was shown that this Bi-D24C8/Nafion SPCE exhibits a remarkably improved sensitivity. Various experimental parameters were optimized to improve the ability of Bi-D24C8/Nafion SPCE to detect Pb^{2+} and Cd^{2+} . Then, the newly proposed method was applied for the determination of Pb^{2+} and Cd^{2+} in rice and rice product samples.

2. Experimental

2.1. Chemicals and reagents

Standard solutions of Pb^{2+} and Cd^{2+} were prepared fresh each day by the appropriate dilution of the stock standard solution (1000 mg dm^{-3} atomic absorption analysis standard solution) purchased from BDH (Poole, England) with 0.5 mol dm^{-3} hydrochloric acid (HCl) solution. The Bi^{3+} plating solution was prepared by the appropriate dilution of the stock standard solution of

$Bi(NO_3)_3$ (1000 mg dm^{-3} atomic absorption analysis standard solution) purchased from Merck (Darmstadt, Germany) with 0.5 mol dm^{-3} HCl. The 0.5 mol dm^{-3} HCl solution, which served as a supporting electrolyte, was prepared by the dilution of concentrated HCl (analytical grade, 37%, 1.19 g cm^{-3} , Merck) with milli-Q water. Graphite powder (Sigma–Aldrich, Buchs, Switzerland), silver ink and carbon ink (Electrodag® 7019 and Electrodag® PF-407C, Acheson, Michigan, USA) were used for screen-printing of the electrodes. D24C8 and Nafion® perfluorinated polymer (5 wt % solution in a mixture of lower aliphatic alcohols and water) from Sigma–Aldrich (St. Louis, MO, USA) were used as electrode modifiers. A 0.5 wt % Nafion solution was prepared by the dilution of 5 wt % Nafion with dimethylformamide (Sigma–Aldrich).

2.2. Electrode preparation

2.2.1. Preparation of D24C8/Nafion modified carbon ink

Ten mg of D24C8 was dissolved in 0.3 cm^3 of 0.5 wt % of Nafion solution and then 1.0 g of carbon ink and 0.2 g of graphite powder were added and mixed to form the homogenized ink.

2.2.2. Screen-printing of D24C8/Nafion SPCE

Silver ink was printed onto the polyvinyl chloride (PVC) substrate to form the conducting part and dried in an oven (Memmert 100-800, Schwabach, Germany) at 55 ± 0.2 °C for 1 h. The modified carbon ink was then printed onto the silver conducting part and dried in an oven at 55 ± 0.2 °C for 1 h.

2.3. Apparatus

A SIA system (MGC Auto-Pret MP-014s, MGC, Japan), which consists of an 8-port selection valve, a 5.0 cm^3 syringe pump and a 5 cm^3 holding coil, and is computer-controlled using the MGC LMPPro ver.2.5 software, was used to deliver the samples and reagents. Square wave ASV (SWASV) measurements were carried out with a potentiostat (eDAQ, Australia) in a thin-layer flow cell (BAS, USA) that consisted of a gasket as a spacer, a D24C8/Nafion SPCE as the working electrode, a silver/silver chloride (Ag/AgCl, 3 mol dm^{-3} KCl) reference electrode, and a stainless-steel tube counter electrode as well as a solution outlet of the flow cell. All SWASV experiments were performed in a laboratory-made Faraday cage at conditioned room temperature. The results from this method in the sample analysis were validated with the ICP-OES (Thermo Scientific, USA).

2.4. SIA–SWASV procedure

The sample solution (Pb^{2+} and Cd^{2+}) and the Bi^{3+} plating solution were sequentially aspirated into the holding coil and dispensed in reverse direction into a thin-layer flow cell in which Bi and the analyte metals were deposited on the working electrode at -1.2 V vs. Ag/AgCl for 180 s. After a 15 s equilibration time at stopped-flow, the voltammogram was recorded from -1.2 to 0.0 V vs. Ag/AgCl by applying a potential with a SW waveform with a frequency of 70 Hz, a step potential of 7 mV and a pulse amplitude of 50 mV. Finally, the electrode was cleaned to remove any remaining analyte metals and Bi film by applying a $+0.4$ V vs. Ag/AgCl potential and a flowing 0.5 mol dm^{-3} HCl solution for 40 s. All experiments were performed in nondeaerated solutions.

2.5. Sample preparation

Two samples of retail rice (sticky brown and Jasmine white rice) and two samples of rice products (wheat rice germ and brown rice milk) were purchased from a local supermarket and analyzed. The

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