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Anti-fouling *In situ* Deposited Antimony/Nafion Film Electrode for Electrochemical Stripping Analysis

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An antimony film electrode for anodic stripping voltammetric analysis in complex solution was investigated, with lead and cadmium employed as test metal ions. Ascorbic acid or dopamine, which exist in most mammals and their metabolites in relatively high concentrations, interfere with the determination of metal ions by electrochemical stripping analysis. The influence of ascorbic acid and dopamine on the stripping voltammetric response of antimony film electrodes was evaluated. The adsorption of these biomolecules onto the electrode caused decreased and non-distinguishable stripping peaks. The interference of the biomolecules on antimony stripping electrodes can be overcome by Nafion pre-coating. In situ deposited antimony/Nafion-coated glassy carbon electrodes exhibited higher sensitivity for electrochemical stripping analysis of cadmium and lead with limit of detection approximately 0.015 μg L-1 in the presence of ascorbic acid or dopamine. The effective anti-fouling capability to ascorbic acid or dopamine makes the in situ deposited antimony/Nafion-coated electrode very attractive for direct measurements of trace metals in complex media.

Keywords: anodic stripping voltammetry, antimony film electrode, anti-fouling, ascorbic acid, dopamine

1. INTRODUCTION

Anodic stripping voltammetry (ASV), an effective pre-concentration step that is followed by electrochemical measurement of the accumulated analytes, has long been recognized as a powerful technique for trace and ultra-trace analysis of heavy metals and some organic compounds [1-3]. Mercury electrodes, including the hanging mercury drop electrode and mercury film electrode, have been widely used for ASV analysis over the past decades [4-8]. However, because of the toxicity of mercury research, efforts have been devoted to alternate electrode materials. ‘Non-mercury’ electrodes, including gold, carbon, iridium, silver or bismuth electrodes, have thus been developed [2, 9-15]. Of the non-mercury electrodes, antimony film electrodes offer remarkable performance in more acidic solutions, and have been proposed for application in trace metal analysis by Hocevar et al. [16]. Recently, there have been reports on the usage of antimony film electrodes for determination of tin ion (Sn^{2+}) in the presence of cetyltrimethylammonium bromide [17], *in situ* preparation on the surface of the carbon paste electrode for ASV analysis of Cd(II) and Pb(II) [18], and fabrication by photolithography for assay of Ni(II)[19]. As a relatively new electrode material for ASV analysis, it is important to understand the factors that influence favorable stripping performance of the antimony film electrode.

For complex environmental, clinical, or industrial samples in practical application, electrochemical stripping analysis suffers from interferences that affect its accuracy and precision [20-22]. A difficulty in the practical utility of ASV is the presence of bioactive molecules, such as ascorbic acid (AA) and dopamine (DA), which exist in most mammals and their metabolites in relatively high concentrations (about 10−4 and 10−6 M, respectively), adsorbed on the surface of the working electrode as surfactants due to physical adsorption or static [23-25]. The adsorption impacts both the pre-concentration deposition and stripping steps. These effects can result in electrochemical signal decrease, peaks becoming broader and the peak potential shifting during ASV determination. The effects of surface active molecules adsorbed on mercury or bismuth film coated electrodes have been well investigated [26, 21]. Interfacial properties of bismuth-film electrodes were reflected in the extent to which these effects depended upon the specific surfactant and the target metal [27, 28].

The goal of the present study was to decrease the influence of ascorbic acid and dopamine on the ASV response by developing Nafion-coated antimony electrodes that combine the attractive features of antimony films with the anti-fouling action of Nafion coating. The results demonstrated that the Nafion-coated antimony electrode exhibited higher sensitivity for electrochemical stripping analysis of cadmium and lead. The combination of a mercury-free stripping electrode with a protective polymeric layer enables direct measurements of trace metals in complex media.

2. MATERIALS AND METHODS

2.1. Materials

Antimony, cadmium and lead standard stock solutions (1000 mg L^{-1}, Atomic Absorption Standard solutions) and Nafion (5% w/v solution in a mixture of water and lower alcohols) were purchased from Aldrich (St. Louis, MO, United States). Working metal ion solutions were prepared from the 1000 mg L^{-1} standard solutions by appropriate dilution with water. A 0.01 M solution of hydrochloric acid (pH 2) served as the supporting electrolyte. All other chemicals were of analytical grade purity, and all solutions were prepared with double-distilled water.

2.2. Methods

2.2.1. Antimony-Nafion film electrode preparation

A glassy carbon (GC) electrode was polished sequentially with 1.0 and 0.3 mm alumina slurries then sonicated in distilled water, ethanol and distilled water for a few minutes. The cleaned GC electrode was dried in a stream of high purity nitrogen. A 10 μL pipette was used to cast 5 μL of the Nafion solution onto the surface of the GC electrode, to obtain the Nafion film modified electrode. The electrode was covered with a beaker, in a refrigerator, so that the solvent evaporated slowly and a uniform film was formed.

Anodic stripping voltammetry was performed by *in situ* co-deposition of the antimony film on the bare (SbFE) or Nafion-coated (Sb/Nafion FE) GC working electrode. Following the electrochemical deposition step and 15 s of equilibration, a square-wave voltammogram was recorded by applying a square-wave potential scan toward more positive potentials. Before each measurement, a “cleaning” step was performed by keeping the working electrode at +0.3 V for 30 s. The three electrodes were immersed in the 10 mL electrochemical cell containing 0.01 M hydrochloric acid (pH 2), 50 μg L^{-1} of antimony and the target metals. The deposition potential (usually -1.2 V) was applied to the glassy carbon or Nafion-coated working electrode for 180 s, while the solution was stirred. Following the pre-concentration step stirring was stopped, and after 10 s the voltammogram was recorded by applying a positive-going square-wave voltammetric potential scan with frequency 30 Hz, amplitude 25 mV and potential step 5 mV. The scan was terminated at +0.30 V. A cleaning step (15 s at 0.3 V, with stirring) was used to remove the target metals and antimony prior to the next cycle.

2.2.2. Apparatus

Stripping voltammetry was performed with a CHI 440 (CHI Instruments Inc., Austin, USA) instrument. A conventional three-electrode cell was used, covered by a Teflon lid. A glassy carbon (GC) electrode (CH Instruments, 3 mm in diameter), and Nafion film modified GC served as the working electrode, with an Ag|AgCl (3 M NaCl) electrode and platinum wire acting as the reference and counter electrodes, respectively. A rotator was used during the pre-concentration and cleaning steps.

3.RESULTS AND DISCUSSION

3.1. Fouling of ascorbic acid and dopamine on glassy carbon electrode surface.

Fig. 1 shows the effect of ascorbic acid and dopamine upon the ASV response of *in situ* plated antimony film electrodes. As expected [20, 33] the electrode displayed well-defined cadmium and lead peaks in the absence of ascorbic acid and dopamine, with peak potentials -0.68 V (Cd) and -0.51 V (Pb). The presence of the ascorbic acid had a deleterious effect upon the response of the antimony film electrode to Cd(II) and Pb(II). The changes include a shift of the peak potentials and substantial diminution of the peak currents. Both anodic stripping peaks for Cd(II) and Pb(II) broadened and interfered with each other, and it was difficult to separate the two peaks. Similar effects were observed in the presence of dopamine. The data did not show the expected correlations with concentration, and could not be used for the determination of Cd(II) and Pb(II). Those phenomena show that the presence of ascorbic acid and dopamine strongly interferes with the stripping analysis determination on the bare GC electrode which can be convinced by others.

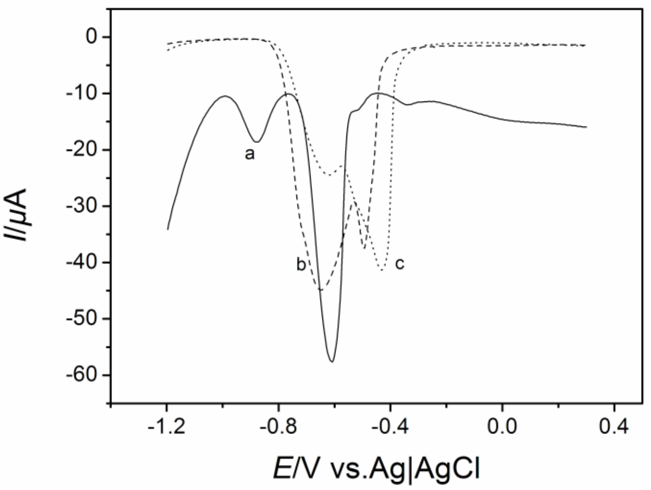


Figure 1. Anodic stripping voltammograms of Cd(II) and Pb(II) at *in situ* prepared antimony film on bare GC electrode. Solution: 0.01 M hydrochloric acid (pH 2) containing 50 μg L^{-1} Cd(II) and Pb(II) together with 0.5 mg L^{-1} Sb(III) (a), in the presence of 50 μmol l^{-1}ascorbic acid (b), and 50 µmol L^{-1} dopamine (c). Deposition at -1.2 V for 120 s, equilibration period of 15 s. Square-wave voltammetric stripping scan with frequency 25 Hz, potential step 4 mV, and amplitude 25 mV.

3.2. Nafion-Coated Antimony Film Electrodes

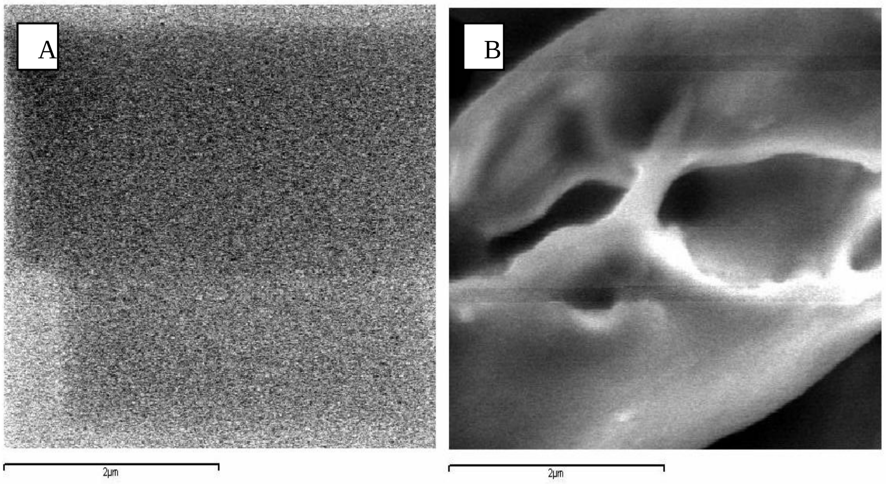


Figure 2. SEM images of the surface of (a) a Nafion-covered glassy carbon wafer electrode, (b) a Nafion-covered glassy carbon wafer electrode plated with antimony.

The microstructure of electrodeposited antimony film on the Nafion-coated GC electrode was observed using scanning electron microscopy (SEM). The GC electrode modified with a Nafion coating (the SEM image is shown in Fig. 2 a), was immersed in a solution of 1 mg L^{-1} Sb(III), and antimony plated by cyclic voltammetry between -1.3 and -1.2 V for 20 cycles. The SEM image of the antimony coating on the Nafion-covered electrode (Fig. 2 b) revealed that the accumulated antimony film was relatively, but not entirely, uniform in terms of the thickness over the surface. In fact, there were protuberances in the film that could be observed from unmagnified images of the electrode surface.

Nafion-modified antimony electrodes were prepared by *in situ* plating of antimony (along with the test metals) onto the Nafion-coated GC electrode. The average antimony film thickness, l_{sb}, was calculated using eq. 1 [22, 33, 34] though the film was not entirely uniform:

$$l_{Sb}=m_{Sb}/A_{SbFE}=Q_{Sb}M_{Sb}/(nF\pi r^2\rho_{Sb}) \qquad (1)$$

where m_{sb} is the amount of metallic antimony deposited on the electrode surface, A_{SbFE} is the area of SbFE, Q_{sb} is the charge for antimony deposition, M_{sb} is the formal weight of antimony (121.75 g mol^{-1}), n is the number of electrons per molecule of antimony during Sb(III) reduction, F is the Faraday constant (96485.3 C mol^{-1}), r is the electrode radius (1.5 mm), and ρ_{Sb} is the density of metallic antimony (6.68 g cm^{-3}).

The charge for antimony deposition and the mass of antimony deposited were calculated by integrating the antimony stripping peak. In the presence of the Nafion coating, the amount of antimony deposited on the electrode surface from a solution containing 50 μg L^{-1} antimony was about 1.75×10^{-10} mol (for 120 s deposition) and the average antimony film thickness on the electrode was about 0.45 nm.

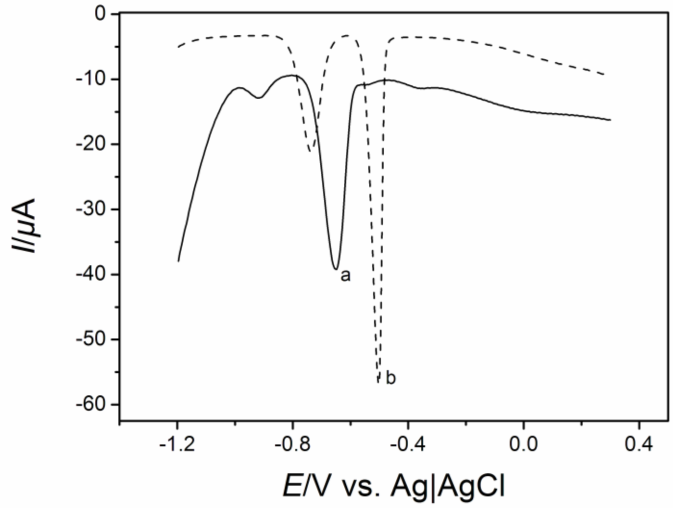


Figure 3. Anodic stripping voltammograms of Cd(II) and Pb(II) at (a) *in situ* prepared SbFE, and (b) Sb/Nafion FE electrodes. Solution: 0.01 M hydrochloric acid (pH 2) containing 50 μg L^{-1} Cd(II) and Pb(II) together with 0.5 mg L^{-1} Sb(III). Parameter values for deposition as in Fig1.

Figure 3 compares the ASV response of Cd(II) and Pb(II) on the SbFE and Sb/Nafion FE electrodes. The ASV response, in terms of either peak current or peak separation for Cd(II) and Pb(II) on Sb/Nafion FE, was better than on the bare GC electrode. The constituent currents for lead and cadmium were higher and the sensitivities for the two metals were enhanced by factors of 1.5 and 2.9, respectively, which is attributed to the more efficient re-plating of lead and cadmium at the end of the forward pulse as the Nafion film helped confine the cationic oxidized species close to the electrode surface. By contrast, on the bare SbFE surface the oxidized species were able to diffuse away from the electrode surface before significant re-plating occurred. Consequently, a synergistic effect of redox cycling and cation exchange pre-concentration, both due to the presence of the Nafion film, may account for the increase in sensitivity on the Sb/Nafion FE electrode relative to the bare SbFE electrode.

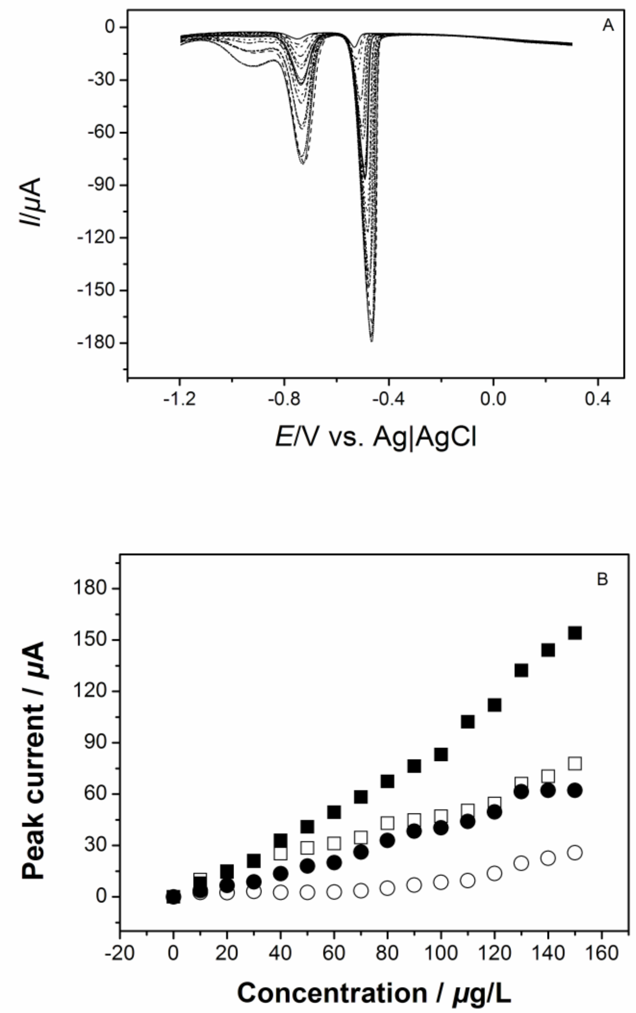


Figure 4. (A) Anodic stripping voltammograms for successive additions of Cd(II) and Pb(II) in 10 μg L^{-1} steps at an *in situ* prepared Sb/Nafion FE electrode. Solutions: 0.01 M hydrochloric acid containing increasing levels of Cd(II) and Pb(II) from 10 to 140 μg L^{-1} together with 0.5 mg L^{-1} Sb(III). **(B)** Variation of peak current vs. the concentrations of Cd(II) (circles) and Pb(II) (squares) with concentration at *in situ* prepared SbFE (unshaded) and Sb/Nafion FE (shaded) electrodes.

Fig. 4 shows that the Sb/Nafion FE electrode revealed good linear behavior for both metal ions, with R^2 of 0.991 and 0.992 for Cd(II) and Pb(II), respectively, in the concentration range 10 to 150 µg L^{-1} after a 120 s deposition step, without cross disturbance, during simultaneous measurements of both analytes. The calculated limit of detection (0.05 µg L^{-1}) for both Cd(II) and Pb(II) was obtained following 120 s deposition time, while repetitive measurements gave relative standard deviations (RSD) of 2.6% for Cd(II) and 6.5% for Pb(II) (150 µg L^{-1}, n=15). For SbFE the detection limit was 0.5 µg L^{-1} for both metals, confirming that the *in situ* prepared Sb/Nafion FE electrode had superior characteristics to SbFE for electrochemical stripping.

3.3. Anti-fouling effect of Nafion-coated electrode

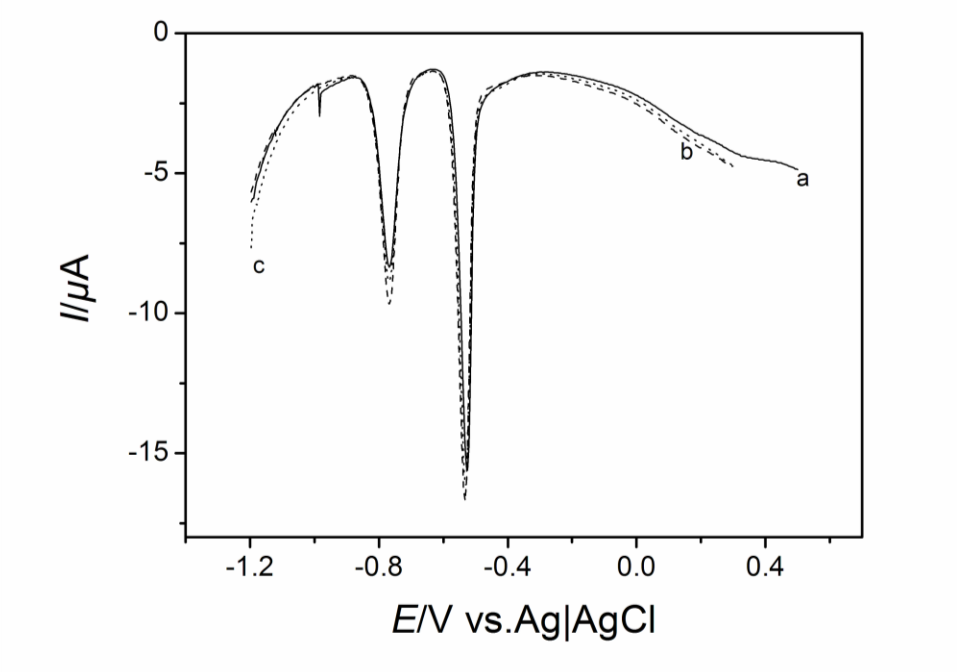


Figure 5. Anodic stripping voltammograms of 10 μg L^{-1} Cd(II) and 10 μg L^{-1} Pb(II) at *in situ* prepared Sb/Nafion FE electrode in the presence of increasing levels of ascorbic acid: (a) 50 μmol L^{-1}, (b) 100 μmol L^{-1}, (c), 150 μmol L^{-1}; in 0.01 M hydrochloric acid (pH 2) containing 50 μg L^{-1} Cd(II) and Pb(II) together with 0.5 mg L^{-1} Sb(III).

The biomolecular fouling effect, observed at the antimony stripping electrodes, can be avoided by using a permselective coating that provides an effective barrier on the electrode surface. Nafion is a perfluorosulfonate cation exchange polymer with ideal properties as a permselective membrane. Its particular characteristics of electroinactivity, chemical inertness, hydrophilicity and insolubility in water enable its broad applications for electrode modification. It was first introduced in ASV measurements of trace metals by Hoyer et al. [26, 35, 36]. Subsequently it has been widely applied in conjunction with the mercury film electrode in ASV, to increase the resistance of the electrode to fouling by surface active compounds [29-32]. Nafion coatings are also highly compatible with antimony electrodes, and impart excellent protection to their surfaces. Figure 5 displays the influence of ascorbic acid on the response of Nafion-coated antimony electrodes. Highly stable cadmium and lead responses were observed while the ascorbic acid concentration changed. There was almost no observable change in the stripping peak position and peak current for both Cd(II) and Pb(II). As expected, the polymeric film forms an effective barrier to adsorption of ascorbic acid on the electrode surface.

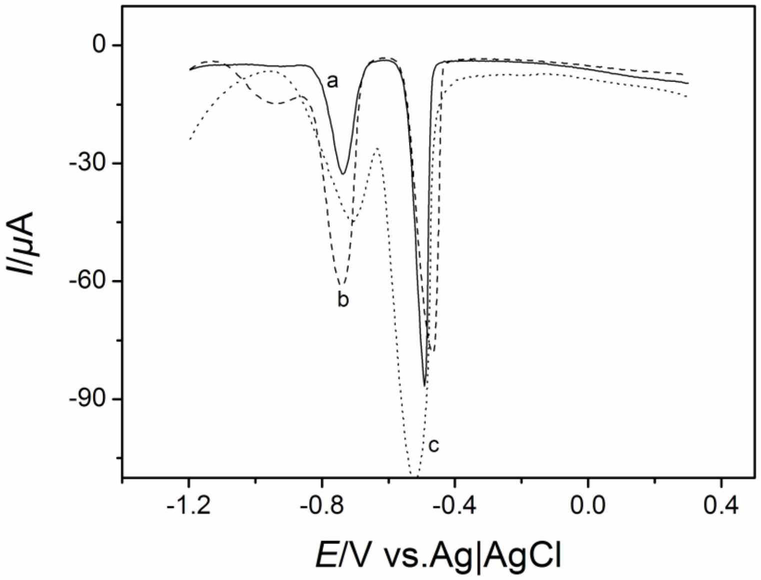
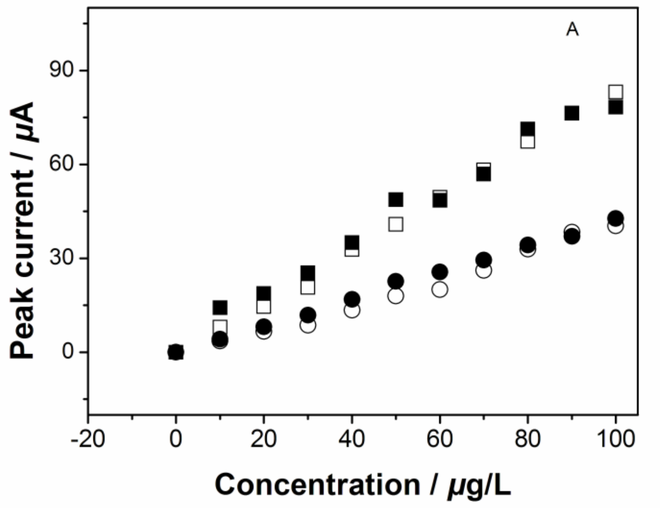


Figure 6. Anodic stripping voltammograms of Cd(II) and Pb(II) at *in situ* prepared Sb/Nafion FE electrode. Solution: 0.01 M hydrochloric acid (pH 2) containing 50 μg L^{-1} Cd(II) and Pb(II) together with 0.5 mg L^{-1} Sb(III) (a), in the presence of 50 μmol L^{-1} ascorbic acid (b) and 50 μmol l^{-1} dopamine (c).

The ASVs of Cd(II) and Pb(II) on *in situ* prepared Sb/Nafion FE electrode in the presence of ascorbic and dopamine are shown in Fig. 6. Though not as perfect as in the absence of the biomolecules (curve (a)), the peaks for Cd(II) and Pb(II) in curves (b) and (c) were clearly separated (ΔE=0.28 mV in (b), and 0.2 mV in (c)). A comparison of peak currents in ASVs of Cd(II) and Pb(II) at an *in situ* prepared Sb/Nafion FE electrode as a function of concentration, in the absence and presence of 50 μmol L^{-1} dopamine or 50 μmol L^{-1} ascorbic acid is shown in Fig. 7. Linear relationships were obtained with good correlation coefficients for the two species, showing that the Sb/Nafion FE electrode is suitable for trace cadmium and lead analysis. The reproducibility of the measurements was also investigated. Repeated sets of fifteen replicate measurements performed at the 5 and 10 μg L^{-1} levels for cadmium and lead, respectively, gave reproducible values within 5%. The detection limit of 0.015 μg L^{-1} for both Cd(II) and Pb(II) was obtained following a 120 s deposition time, while repetitive measurements gave an RSD of 3.0% for Cd(II) and 3.9% for Pb(II) (140 μg L^{-1}, n=13) in the presence of dopamine, and 4.5% for Cd(II) and 2.8% for Pb(II) in the presence of ascorbic acid. All of the results demonstrated that the Nafion film effectively prevented fouling by the biomolecules.



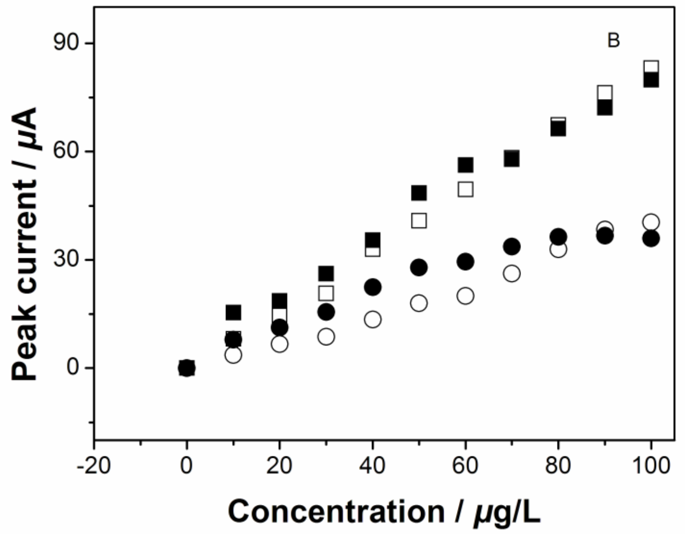


Figure 7. **(A)** Variation of peak current in anodic stripping voltammograms of Cd(II) (circles) and Pb(II) (squares) with concentration at an *in situ* prepared Sb/Nafion FE electrode (unshaded) and in the presence of 50 μmol L^{-1} dopamine (shaded). **(B)** Corresponding data obtained in the presence of 50 μmol L^{-1} ascorbic acid (shaded).

4. CONCLUSIONS

An *in situ* deposited antimony/Nafion film electrode has been successfully developed for anodic stripping voltammetric analysis of lead and cadmium in complex solution. Ascorbic acid and dopamine, which exist in most mammals and their metabolites in relatively high concentration, interfere with the determination of metal ions using the electrochemical stripping analysis method. The influence of ascorbic acid and dopamine on the stripping voltammetric response of antimony film electrodes was characterized by decreased and non-distinguishable stripping peaks for lead and cadmium. The interference of biomolecules at antimony stripping electrodes can be overcome by Nafion pre-coating. ASV analysis on Nafion film modified antimony film electrode was used to minimize the problem. We have demonstrated that the *in situ* deposited Sb/Nafion FE electrode exhibited higher sensitivity for electrochemical stripping analysis of Cd(II) and Pb(II) with a detection limit of approximately 0.015 μg L^{-1} in the presence of ascorbic acid or dopamine, whereas the unmodified antimony film electrode showed no separation of ASV peaks for the metals. The effective anti-fouling to ascorbic acid and dopamine makes the *in situ* deposited Sb/Nafion FE system very attractive for practical stripping applications.

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