



Submonolayer deposition on glassy carbon electrode for anodic stripping voltammetry: An ultra sensitive method for antimony in tap water

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ABSTRACT

Atomic layers of antimony were electrodeposited onto glassy carbon electrode in overpotential region. The antimony deposition was characterized by chronocoulometry and scanning electron microscopy. Based on the excellent electrochemical properties of the glassy carbon/antimony system, a simple method was developed for rapid and reliable determination of ultra-trace Sb(V) by square-wave anodic stripping voltammetry. The key operational parameters of influencing the electroanalytical response of Sb, such as deposition potential, deposition time, and composition of the measurement solution, were investigated. Under the optimized condition, the method provided a linear calibration ranging from 1 to 16 $\mu\text{g L}^{-1}$ with a respective correlation coefficient of 0.9906. The detection limit was 1.64 fmol L^{-1} , which is the lowest ever reported for an electroanalytical technique and one of the lowest analytical methods for Sb(V) determination. The relative standard deviation for a Sb(V) solution (5 $\mu\text{g L}^{-1}$) was 3.2% for eight successive assays. Finally, the method was applied to the determination of antimony in tap water and compared with inductively coupled plasma mass spectrometry technique.

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1. Introduction

Antimony (Sb) is a metalloid element that occurs naturally due to rock weathering, soil run-off and atmospheric deposition in the environment. However, its presence in the environment is also caused by various anthropogenic activities. Industrially, antimony is used in the fabrication of lead alloys, fire retardants, glassy and ceramics, batteries and polyethylene terephthalate as a polycondensation catalyst [1,2]. Normal concentrations of antimony in water sources vary from a few ng L^{-1} to a few mg L^{-1} , depending on localization and/or anthropogenic activity. Typical levels in rivers and lakes are $<8 \text{ nM}$ ($\sim 1 \text{ ppb}$) but can be as low as 0.2 ng L^{-1} in pristine ground waters [1,3]. The two common inorganic forms of

antimony present in surface water are antimonate (Sb(OH)_6^-) and antimonite (Sb(OH)_3). The inorganic oxidized Sb(V) species are predominant in oxic waters (with 70–94% of the total antimony being present as Sb(V) species), the reduced Sb(III) species occurring at much lower levels due to biotic and abiotic reduction processes coupled with slow oxidation kinetics [4].

The ecotoxicity of antimony is considered poisonous to humans and animals at high dosage with marked similarities to the toxic nature of arsenic [5]. Antimony and its compounds are listed as pollutants of priority interest by the United States Environmental Protection Agency and the Council of the European Communities, which have considered a maximum contaminant level of antimony in drinking water of $5\text{--}6 \mu\text{g L}^{-1}$ [6,7]. Therefore, developing sensitive and selective methods for the determination of antimony in various samples is of great importance.

The determination of antimony in various sample matrices can be performed by microwave induced plasma-atomic emission spectrometry [8], inductively coupled plasma mass spectrometry [9], solvent extraction-atomic absorption spectrometry [10], laser induced fluorescence [11] and high performance liquid chromatography [12]. However, the sensitivity of these methods is

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sometimes inadequate to determine ppt or sub-ppt concentration of Sb in environmental samples. Preconcentration is required, which is time consuming, laborious and may cause contamination. Moreover, these techniques are impractical for on-site screening owing to their size and analytical costs. In this aspect, advanced electroanalytical methods provide a favorable alternative offering sensitive and selective measurements associated with relatively simple, portable and non-expensive instrumentation [13].

Stripping voltammetry/chronopotentiometry has been recognized as one of the most convenient choices for measuring trace metal ions. Due to the unique capability of pre-concentrating analytes at/in the working electrode surface, electrochemical stripping analysis allows quantification of, e.g. toxic metal ions down to low microgram per liter or even nanogram per liter concentration levels [14]. Performance of a stripping voltammetric procedure depends primarily on the appropriate choice of the working electrode. Many electrodes, such as, the mercury drop [15–19], mercury films [20], solid gold [21–24], gold films [25], bismuth films [26–28], antimony films [29,30], gold nanoparticles [31], or silver nanoparticles [32], carbon material electrodes [33–35], have been developed. Among them, mercury-based electrodes have been most widely used in the past six decades due to superior electroanalytical performance of mercury, despite of its well-known toxic character and difficulties associated with its handling, storage, and disposal. Carbon materials and bismuth are two most popular materials for electrochemical stripping analysis in recent years. In particular, glassy carbon electrode (GCE) has gained wide acceptance due to its chemical inertness, low sensitivity to memory effects and easy modification.

It has been reported antimony(III) is more toxic than the pentavalent species [36]. However both species are generally found in environmental samples at varying ratios and as such guidelines regarding maximum contaminations consider the total antimony concentration. Electrochemical methods for the determination of total antimony have mostly focused on the detection of Sb(III) because of the perceived electro-inactivity of Sb(V). Prior to research based on depositing beyond the hydrogen wave [24,34], stripping voltammetry to determine Sb(V) requires harsh acidic media or pre-reducing agents to convert all Sb(V) to Sb(III) within the sample solution prior to analysis [28,35,37,38]. The reduction step is time-consuming, might be difficult to implement, and also is a major potential source of contamination at low antimony levels. The high acidic conditions are not appealing for routine use. Up to now, the most sensitive method for Sb(V) detection was achieved by anodic stripping voltammetry on a vibrating gold microwire, with a detection limit of 5 pM after 60 s accumulation time [24].

Underpotential deposition (UPD) is the electrochemical deposition of foreign metals onto substrates at potentials positive relative to the reversible Nernst potential for bulk deposition. During the deposition step, the adatom coverage of trace elements is in the range of 0.01–1% and no bulk deposition is invoked for metals that exhibit UPD [39]. Because UPD is a monolayer phenomenon, the stripping peak of the monolayer usually shows more sharp and reproducible characteristics [40]. UPD was usually achieved with metal electrode, such as Au, Pt, Ag and other materials [39]. To the best of author's knowledge, the experiment of monolayer deposition on unmodified glassy carbon electrode has never been reported.

In the present work, ultra-trace Sb(V) (from 1 to 50 $\mu\text{g L}^{-1}$) was deposited on a glassy carbon electrode in non-deaerated acetate buffer. Then, square-wave anodic stripping voltammetry (SW-ASV) was applied to stripping monolayer of Sb on the electrode. The factors that influence the sensitivity of detection, such as pH of buffer, deposition potential and accumulation time, were optimized. In addition, the interferences from foreign ions were examined. Furthermore, the new protocol was also tested via measurement of

ultra-trace antimony in tap water and compared with the ICP-MS technique.

2. Materials and methods

2.1. Reagents and materials

All chemicals employed in this work were of analytical reagent grade unless stated otherwise. Throughout the experimental work, all solutions were prepared from doubly deionized water obtained by passing through a Milli-Q Millipore laboratory water purification system (Millipore, Bedford, USA). All the experiments were carried out at room temperature (approximately 25 °C) and without removing oxygen. Stock standard solutions of Sb(V) were prepared by dissolving appropriate amounts of potassium hexahydroxy antimonite(V) (Fluka) in hot water. Stock Sb(III) solution was obtained by dissolving potassium antimony tartrate(III) (Aladdin Reagent Co., Shanghai, China) in ethanol. The sample was obtained by diluting the stock standard sample with supporting electrolyte to the desired concentration in 10 mL polyethylene centrifuge tube. Flasks containing Sb(III) standards solutions were wrapped in aluminum foil paper to avoid oxidation. Metal solutions ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2$ and $\text{Bi}(\text{NO}_3)_3$) (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were used for interference experiments; HNO_3 , CH_3COOH (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was analytical reagent grade and used as received; sodium acetate (purity $\geq 99.99\%$) was from Aladdin (Aladdin Reagent Co., Shanghai, China).

2.2. Equipment

Cyclic voltammetry, chronocoulometry and SW-ASV were performed with a CHI-660D electrochemical station (Chenhua Instruments Co., Shanghai, China), in connection with a personal computer. Scanning electron microscopy (SEM) images were obtained using a quanta 200 scanning electron microscopy (FEI, Holland). The MS-H-S meter (Dragon Instrumentation Co. Ltd., China) was used to measure the pH of solution. A conventional three-electrode system consisted of a glassy carbon electrode as the working electrode with a diameter of 3.0 mm, a counter electrode made of platinum wire, and an Ag/AgCl/3 M KCl reference electrode. All electrochemical measurements were carried out in a 20 mL quartz electrochemical cell in a Faraday cage. All potentials were given with respect to the Ag/AgCl electrode. In chronocoulometry and anodic stripping measurements, a Teflon-coated magnetic stirring bar (approximately 300 rpm) was employed during the electrochemical deposition step. The electrodes were stored in air or Milli-Q water. All glassware, polypropylene sample cups and polyethylene bottles, was carefully cleaned by soaking in (1 + 1) nitric acid over 24 h, followed by thorough rinsing with copious amounts of ultrapure water, to avoid accidental contamination.

2.3. Measurement procedure

The bare glassy carbon electrode was polished to a mirror using 0.3 and 0.05 μm Al_2O_3 powder, successively, and rinsed thoroughly with doubly distilled water between each polishing step. Then it was washed successively with 1:1 (v/v) HNO_3 aqueous solution, doubly distilled water, ethanol and doubly distilled water in ultrasonic bath and dried in air. 0.1 M acetate buffer (pH 4.0) was used as the supporting electrolyte except a part of the optimization experiments.

The established procedures for the determination of Sb(V)/Sb(III) by SW-ASV were carried out as follows: 10 mL of acetate buffer solution (0.1 mol L^{-1}) was pipetted into the quartz electrochemical cell and antimony from a stock solution

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