Analysis of As(III) by Anodic Stripping Voltammetry

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Purpose

Anodic stripping voltammetry (ASV) has proved to be a sensitive, precise, and cost-effective electroanalytical technique for determining trace metals [1]. It is routinely used for detecting Pb(II) and Cd(II). Other metals (e.g., Ag, Bi, Cu, Hg, In, Sb, Sn, Ti, and Zn) have been determined at ppb concentration [2]. The general procedure of this technique involves depositing metal(s) at a reductive potential into Hg electrodes for a certain time and stripping them back into the solution by scanning the potential in the oxidative direction. The current due to oxidation of various analytes is obtained as peaks with heights proportional to their concentrations. Use of solid electrodes (e.g., Au, Pt, Ni, and C) has been described [1].

Arsenic exists in two oxidation states, As(III) and As(V), the former being more toxic [3]. Only As(III) is electrochemically active. Therefore, conversion of As(V) to As(III) is necessary for evaluating total As content [4,5]. This, in turn, provides quantitative information about the two forms. Therefore, electrochemical analysis is preferred for the determination of As.

Existing Methods

Determination of arsenic is possible by various methods; spectrophotometry, atomic absorption (as arsine), atomic emission, and neutron activation analysis are common. High levels of interference and the high costs of these methods are major drawbacks [4]. Analysis of As(III) by ASV has been investigated using solid Au and Pt, and Hg drop electrodes [1]; the latter has shown limited success [4]. Solid Au and Pt have given adequate detection limits for As(III) [4,6]. Cathodic stripping voltammetry (CSV) has also been used [5].

Instrumentation

ASV can conveniently be performed with the BASi e2 epsilon. Improved detection limits can be achieved with the differential pulse (DPSV) or square wave (SWSV) stripping modes available with this instrument.

Electrochemical Pretreatment of Gold Electrodes

Electrochemical pretreatment of the gold surface was necessary to achieve consistent results with stable background levels [4]. The electrodes were stored in 6.0 M HNO3. Prior to the analysis, surface oxides were reduced electrochemically by holding the electrode at a potential of 0.0 V in 1.0 M HClO4 until the current dropped to about 5% of the original value. The electrode was rinsed with deionized water before use. This can automatically be done using the epsilon's Constant Potential Electrolysis (CPE) technique (Check: END CONDITION. Ratio –PPT (initial/end) = 50 (ppt or 5%)).

All operating conditions, including the position of the electrode with respect to the stirrer, and the rotation speed, were kept constant to obtain reproducibility in results. The concentrations used were achieved by standard addition of 9.6 µM As(III) solution [4]. Background solution was 1.2 M HCl. The reference electrode and the auxiliary electrode were Ag/AgCl and Pt wire, respectively. The glassware was rinsed with 6.0 M HNO_3 at the beginning of analysis.

Cyclic Voltammetry

Cyclic voltammetry of As(III) at conventional disk and screen-printed (on ceramic substrate) Au electrodes is shown in F1. The reduction of As(III) is represented by two peaks at approximately -30 and -230 mV. Oxidation of As on the reverse scan takes place at about +220 mV. Based on this information, As(III) can be plated close to -100 mV or -300 mV.

Stripping Voltammetry

Differential pulse stripping voltammograms of As(III) in the background solution and the added concentration range of 10-90 ppb is shown in F2. Both conventional disc and screen-printed Au electrodes give a linear response for As(III) when plated at -100 mV. Current per unit geometric area at screen-printed electrodes is much higher. At the present time, EPA-allowed As content in drinking water is 50 ppb. The electrodes employed here provide adequate detection limits, down to a few ppb, with carefully controlled experimental conditions.

Figure 1. Cyclic voltammetry of As(III) at: (a) screen-printed, (b) disc Au electrodes. Scan rate = 50 mV/sec.

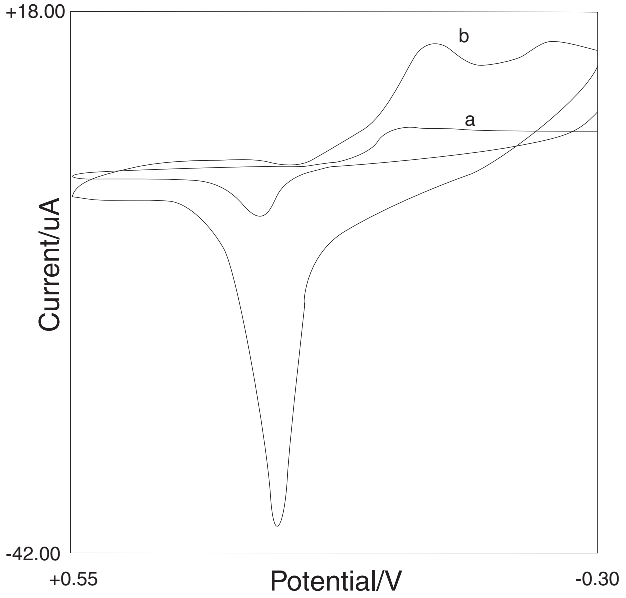
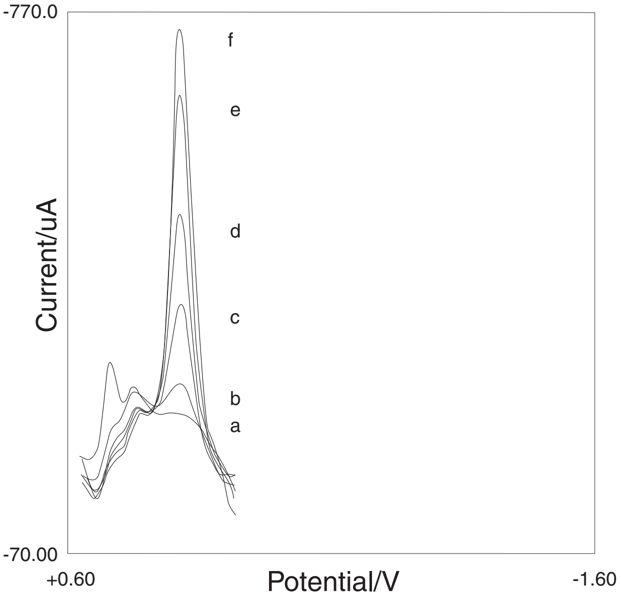


Figure 2. DPSV of As(III) at conventional gold disc electrode. The lowest to the highest peaks are: (a) background, (b) 10, (c) 30, (d) 50, (e) 70, and (f) 90 ppb.



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