

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

All chemicals used are of reagent grade. These compounds were used without further purification unless otherwise stated. Hygroscopic compounds were kept in a desiccator over silica gel. Thrice deionized water and purified N_2 used throughout this study were prepared as described in reference 8.

2.2 Apparatus

Voltammograms and polarograms were obtained with Radiometer Copenhagen Polariter type PO4 g. The cell employed in all stripping analyses is a two compartments cell (H-cell); one compartment served for reference electrode, saturated calomel electrode (SCE) and another compartment for the test solution. Glassy carbon (vitreous carbon rod; $\frac{1}{8}$ " dia., from Bechwith Carbon Corporation) is used as working electrode. The glassy carbon electrode (GCE) used was prepared by modified method of Kanatharana and Spritzer (9); a piece of glassy carbon rod (10 mm long) was glued in a 4 mm (ID) soft glass

tube with Araldit epoxy (Ciba - Geigy Limited, Basle, Switzerland).

In amperometric titration, one compartment cell (ca. 45 cm³ capacity) was used. The reference electrode is a SCE (Radiometer Electrode Model K 501) and the dropping mercury electrode (radiometer Electrode Model B 400) is a working electrode.

All potentials in this work were measured against SCE. The pH measurements were obtained with a pH meter (Radiometer Copenhagen type PHM 28).

2.3 Procedure

2.3.1 Stock solutions

A stock solution of each of these elements, As (III), Sb (III), Bi (III) and Sn (IV) was prepared in a 250 cm³ volumetric flask.

2.3.1.1 As (III) solution

A 0.5005 g of As₂O₃ was dissolved in 86.2 cm³ of conc. HCl and the solution was made up to 250 cm³ with thrice deionized water (this solution contained about 4M HCl). As standardized with 0.0250 M KIO₃(10), the solution has a concentration of 5.00 mM As (III).

2.3.1.2 Sb (III) solution

A 0.5703 g of SbCl_3 was dissolved in 54 cm^3 of conc. HCl and the solution was diluted to 250 cm^3 with thrice deionized water (this solution contained about 2.5 M HCl). The solution as standardized with 0.0250 M KIO_3 (10) gives a concentration of 9.90 mM.

2.3.1.3 Bi (III) solution

A 1.2272 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{ H}_2\text{O}$ was dissolved in 15 cm^3 of 1:1 HNO_3 and the solution was made up to 250 cm^3 with thrice deionized water. The concentration of this solution is 10.00 mM Bi (III) as standardized with 0.0100 M EDTA solution by microvolumetric analysis using xylenol orange as indicator (10) and amperometric titration using modified methods in reference 10 and 11 (ten times dilution of Bi (III) stock solution was used and the pH of the solution was adjusted to 1 - 2 with conc. HNO_3). The mixture was amperometrically titrated with standard 0.0100 M EDTA at -0.15 V).

2.3.1.4 Sn (IV) solution

Dissolved 0.8765 g of $\text{SnCl}_4 \cdot 5 \text{ H}_2\text{O}$ and made the volume up to 250 cm^3 with 2 M HCl. This solution gives 9.32 mM Sn (IV) by gravimetric analysis (10).

2.3.2 Test solutions

Test solutions were obtained by the successive dilution of the appropriate stock solution in a 100 cm³ volumetric flask; As (III) with 6 M HCl, Sb (III) with 1 M HCl, Bi (III) with 0.5 M HNO₃ or 0.06 M HNO₃ and Sn (IV) with 1 M HCl.

2.3.3 Voltammetric and Stripping Analysis

To obtain the deposition potential of each ion solution, a voltammogram of the ion desired must be recorded and the peak potential is measured.

Before the test solution was placed in the cell for either voltammetric or stripping analysis, the test compartment was washed twice with thrice deionized water. The test solution was poured into the test compartment, then deaerated with purified nitrogen for ten minutes by means of a disposable capillary. In order to prevent the redissolution of oxygen a stream of purified nitrogen was maintained over the solution surface during the measurement. Then GCE was inserted in the test compartment. The desired potential range, current sensitivity, scan rate and polarity were set on the instrument and the voltammograms were recorded.

In stripping analysis, before the solution was deaerated, two small pieces of magnetic stirring bars

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were placed in the test compartment and after the GCE was inserted, the deposition potential was set on the instrument and the electrodeposition of the ion was operated in a known limited time. Then the stripping voltammogram was recorded.