CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

All chemicals used are of reagent grade. No further purification of these compounds was attempted unless otherwise stated. Hygroscopic compounds were kept in a desiccator over the anhydrous silica gel. Thrice deionized water and purified N_2 used throughout this study were prepared as described in reference 11.

2.2 Apparatus

Both cathodic and anodic voltammograms were obtained with a Radiometer Copenhagen Polariter type PO 4g. The cell employed in all anodic stripping analyses except that is for Mo is a two compartment cell (H-shaped cell); one compartment served for reference electrode, saturated calomel electrode (SCE), and another compartment for the test solution. In anodic stripping analyses of Mo (VI), a 50 cm^3 polyethylene beaker and a SCE (Radiometer Electrode Model K 501) were used.

The glassy carbon electrode (GCE) with an exposed area approximately 0.071 cm^2, prepared by modified method of Kanatharana and Spritzer (12), served as a working electrode. A piece of 10 mm glassy carbon rod (vitreous carbon rod, $\frac{1}{8}$" dia., from Beckwith Carbon Corp.) was glued in a 4 mm (ID) soft glass tube with Araldit epoxy

(Ciba-Geigy Limited, Basle, Switzerland). A fresh glassy carbon surface was usually prepared before each run by polishing with a piece of silicon carbide paper on a polishing wheel.

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

The stock solution of Mo (VI), W (VI), V (V), and Ti (IV) were prepared in volumetric flasks.

2.3.1.1 1.00×10^{-2} M Mo (VI) solution

A 1.20975 g of $Na_2Mo\ O_4 \cdot 2H_2O$ was dissolved and diluted to 50 cm^3 with thrice deionized water.

2.3.1.2 1.00×10^{-2} M W (VI) solution

Dissolved 0.32986 g of $Na_2WO_4 \cdot 2H_2O$ and make up the volume to 100 cm^3 with thrice deionized water.

2.3.1.3 1.00×10^{-2} M V (V) in 0.2 M HCl solution

According to the limitation of solubility in water and the decomposition in hot water (96°C), ammonium meta vanadate (NH_4VO_3) solution was prepared in acid medium; 0.2 M HCl was found to be the optimum condition. A 0.11698 g of NH_4VO_3 was dissolved in 1.7 cm^3 of concentrated HCl and diluted to 100 cm^3 with thrice deionized water.

2.3.1.4 4.00×10^{-4} M Ti (IV) in 0.5 M H_2SO_4 solution

TiO_2 is soluble only in sulfuric acid and alkali (13). A 30 cm^3 of concentrated H_2SO_4 was added to 0.0799 g of TiO_2 and the mixture was strongly heated to white fume of SO_3. After complete dissolution, the solution was carefully diluted to 250 cm^3 with thrice deionized water.

2.3.2 Test solutions

Test solutions were obtained by the successive dilution of the appropriate concentration of the stock solution desired in a 100 or 50 cm^3 volummetric flask.

2.3.3 Salt bridge and reference electrode

Salt bridge and the SCE were prepared as described in reference 14.

2.3.4 Voltammetric and stripping analyses

In order to obtain the deposition potential of any species, a cathodic voltammogram of the species interested was recorded and the peak potential was 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 and rinsed once with the test solution.

Since oxygen is reduced at potentials more negative than 0.1 volt vs SCE and the resulting current tends to mask

the waves or peak voltammograms, removal of dissolved air from the test solution with nitrogen or carbondioxide is usually necessary (15). Thus,the test solution was deaerated with purified nitrogen for five to ten minutes by means of a disposable capillary. In addition, a stream of purified nitrogen was maintained over the solution surface during the process of analysis. The GCE was then inserted in the test compartment. The desired potential range, current sensitivity, scan rate and polarity were set on the equipment and the voltammogram was recorded.

In stripping analysis, before the test solution was deaerated two small pieces of magnetic stirring bars (ca. 1 cm long) were placed in the test compartment and after the GCE was inserted, the deposition potential was set and the electrodeposition of the species was operated in a known limited time. Then the anodic stripping voltammogram was recorded.