CHAPTER 4

ANODIC STRIPPING ANALYSIS OF TUNGSTEN

Tungsten had been determined polarographically in 1-12 M H_3PO_4 (18, 49); in 0.2 M sodium oxalate containing 0.005% gelatin, pH 0.5 to 1 (50); and in saturated sodium chloride solution containing 0.001 M HCl and 0.005% gelatin (51). The polarographic behavior of W (VI) was studied in 1-10 N HCl or H_2SO_4 and 0.2 N or 0.4 N oxalic acid (52), and in 8-20 M H_3PO_4 or 4.0 - 10.0 M $H_4P_2O_7$ at $25^\circ C$ and $85^\circ C$ (53). Amperometric titration of W (III) with K_3Fe $(CN)_6$ (54, 55) was reported. Moreover, the indirect potentiometric titration of tungsten with standard sodium sulfite solution (32) and with standard $K_2Cr_2O_7$ solution (55) was demonstrated.

Oscillopolarographic determination of tungsten in 4 N to 5 N HCl with no interference from Mo, Ti, and Nb (56, 57, 58); in niobium alloys in the presence of 8 M HCl (42); and in saturated tartaric acid with a scan rate of 4 V/sec (42, 43) were reported. Simultaneous determination of tungsten and tin in HCl and tartaric acid without the interference from Fe(III) and Mo was also employed (59, 60). A lower limit of detection of 3.00 X 10^{-7}M W (VI) was possible by inverse polarography (46). In addition, the cathodic behavior of some tungsten (VI) compounds on the carbon paste electrode and HCl as supporting electrolyte was described (61).

4.1 Evaluation of Electrolyte

4.1.1   0.02 M acetic acid and 0.02 M acetate in 0.10 M NaCl solution.

According to the existence of molybdenum and tungsten in the same group (group VI B of the periodic table) and their simi-larities in chemical properties, the electrolyte containing 0.02 M acetic acid and 0.02 M sodium acetate in 0.10 M NaCl was tried. A cathodic peak occurs at the potential of -1.37 V. After electrode-position at -1.40 V, an anodic peak at -0.84 V is shown. It is evident that the anodic peak does not result from the first anodic stripping voltammogram, however, it is shown in the second, and third voltammogram. Since high charging current is obtained in the anodic stripping voltammogram the anodic peak current cannot be measured.

Even the sequence for preparing the test solution is alternated: adding acetate buffer (equiamount of acetic acid and sodium acetate) to the appropriate amount of W (VI), and following with the appropriate amount of NaCl solution, then diluting to the mark of the volumetric flask used, the charging current in anodic voltammogram is still high and the peak current cannot be measured.

4.1.2   Acetate buffer

The voltammetric behavior of tungsten in 0.02 M acetic acid and 0.02 M acetate solution (pH 4.60) is first investigated. A cathodic peak is obtained at ca. -1.64 V and an anodic peak is shown

in the stripping voltammogram after electrodeposition for 10 minutes.

The effect of pH on the cathodic voltammogram and the anodic stripping voltammogram of tungsten is studied and the results are concluded in Table 6. It has been seen in anodic voltammograms of tungsten that the higher the pH is the more negative peak potential is obtained and the maximum peak current exhibits at pH 3.

Table 6 Effect of pH on the voltammetric behavior of tungsten[a]

pH^b	CH_3COOH (M)	CH_3COONa (M)	$E_{p,c}$ (V)	$E_{p,a}$ (V)	$i_{p,a}$ (μa)
2.70	0.20	none	none	-0.07	12.90
2.75	0.20	none	none	-0.07	17.90
3.00	0.20	0.004	ca.-1.90	-0.07	18.58
4.00	0.02	0.004	-1.97	-0.13	11.60
4.60	0.02	0.02	-1.63	+0.25	2.95
5.00	0.02	0.036	-1.46	none	none
8.10	none	0.20	none	none	none

[a]
using 5.00 X 10^{-4} M W (VI) and electrodeposition at -2.0 V for 10 minutes.

[b]
pH of test solution before the performance of cathodic analysis and anodic stripping analysis.

4.1.3 Other electrolytes

Cathodic voltammetric behavior of W (VI) in the follow-
ing electrolyte is studied: 0.2 M sodium oxalate, 0.1 M sodium tar-
trate in the presence of 4 M HCl, 1, 2, 3 M H_3PO_4, and 4 M HCl. No
cathodic peak is observed. Thus, the deposition potential for W (VI)
in these electrolytes cannot be obtained and no anodic stripping
analysis of W (VI) in these electrolytes is studied.

Therefore, the anodic stripping analysis of W (VI) at
the GCE is studied in the acetate buffer at pH 3.

4.2 Stripping Analysis

Since the cathodic peak potential of W (VI) in acetate buffer
at pH 3 is ca. -1.90 V, the deposition potential of -2.00 V is
selected. Many periods of time for electrodeposition are performed
corresponding to the concentration of W (VI). Conditions for electro-
deposition of W (VI) in acetate buffer at pH 3, data of stripping
analysis, and the detection limit are given in Table 7. It has been
observed that some bubbles of gas evolve at the surface of GCE during
the time of electrodeposition of W (VI).

A single peak at ca. -0.20 V is shown in the anodic voltam-
mogram after either 5-minute-deposition or 10-minute-deposition of
2.00×10^{-5}M to 1.00×10^{-4}M W (VI) (see Figure 4 A). The peak cur-
rents obtained from anodic stripping analyses of W (VI) in the range
of concentration 2.00×10^{-5}M to 1.00×10^{-4}M, using 5 minutes for

Table 7 Conditions for deposition of W (VI) and data of stripping analysis of tungsten in 0.2 M CH_3COOH + 0.004 M CH_3COONa, pH 3.0

Deposition		Conc of W(VI) (M)	$i_{p,a}$ [a] (μa)	$E_{p,a}$ (V)	Detection limit (M)
Potential (V)	time (min)				
-2.00	5	1.00×10^{-4}	2.87 ± 0.28	-0.20	
		8.00×10^{-5}	1.28 ± 0.38		
		6.00×10^{-5}	0.54 ± 0.00		
		4.00×10^{-5}	0.27 ± 0.01		
		2.00×10^{-5}	0.13 ± 0.01		
-2.00	10	1.00×10^{-4}	5.22 ± 0.17	-0.16	
		9.00×10^{-5}	4.21 ± 0.38		
		8.00×10^{-5}	2.85 ± 0.30		
		7.00×10^{-5}	2.47 ± 0.27		
		6.00×10^{-5}	1.45 ± 0.14		
		5.00×10^{-5}	0.90 ± 0.04		5.00×10^{-5}
-2.00	20	1.25×10^{-5}	8.41 ± 1.11	+0.04	
		1.00×10^{-6}	5.70 ± 0.42		
		7.50×10^{-6}	5.01 ± 0.28		
		5.00×10^{-6}	2.56 ± 0.34		
		2.50×10^{-6}	1.50 ± 0.18		2.50×10^{-6}

[a] average anodic peak current $\pm$ average deviation of more than 4 trials.
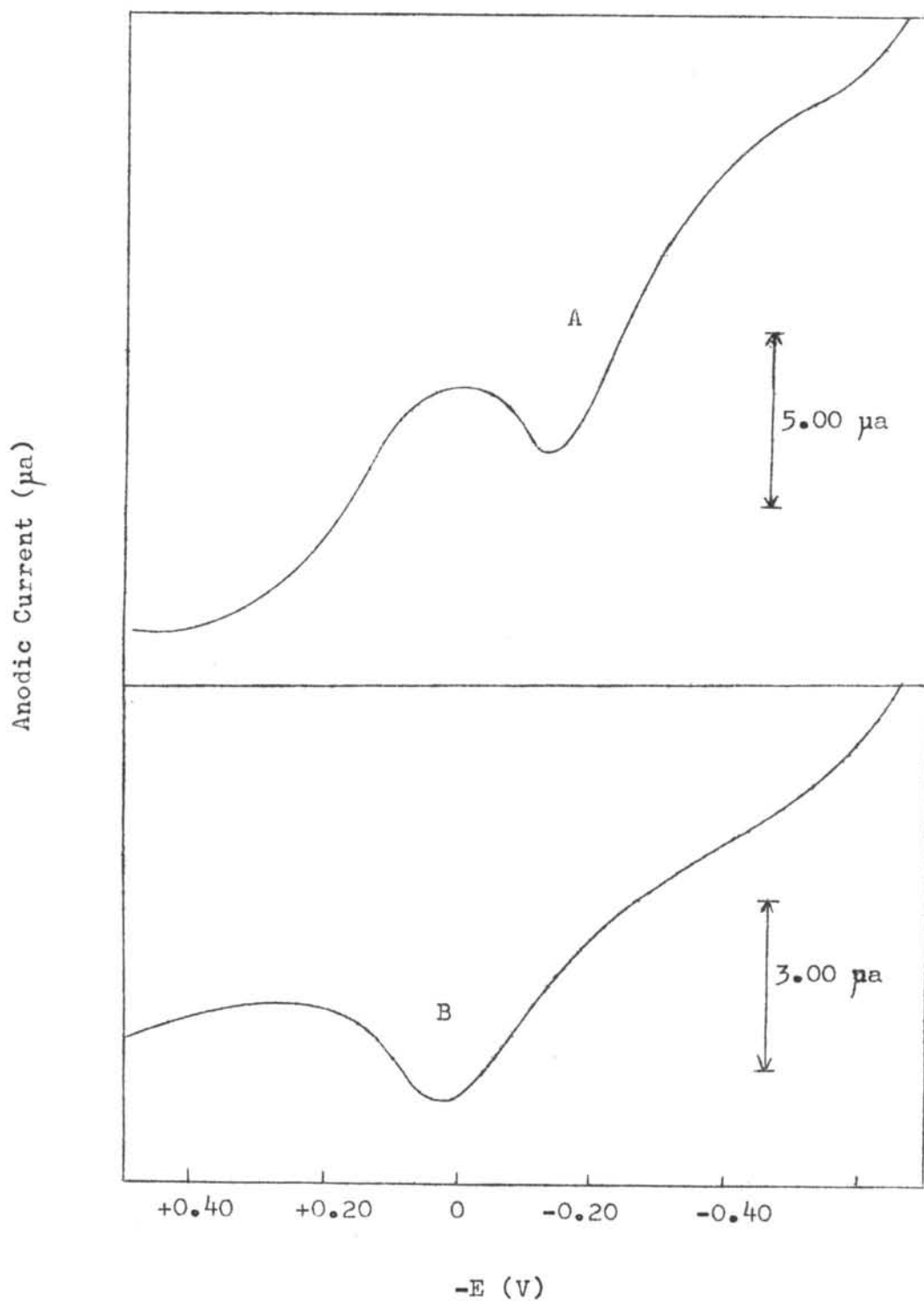
Figure 4 Anodic voltammograms of tungsten after deposition of A) 9.00 X 10^{-5}M W (VI) for 10 minutes, and B) 5.00 X 10^{-6}M W (VI) for 20 minutes.

electrodeposition, slightly change (see Figure 5 A). Thus, 5-minute-deposition of 2.00×10^{-5}M to 1.00×10^{-4}M W (VI) gives lower sensitivity. The 10-minute-deposition has been tried and the higher peak current is obtained. In addition, the peak current is proportional directly to the concentration of W (VI) (see Figure 5 B). For 20-minute-deposition of W (VI), a single peak at the potential of +0.04 V exhibits in the anodic voltammogram (see Figure 4 B). This means that a new anodic species is occurred. It could be that the anodic species at the potential of ca. -0.20 V is oxidized to this new species which has the higher oxidation state (more positive peak potential). The linear dependence of anodic peak current on the concentration of 2.50×10^{-6}M to 1.25×10^{-5}M W (VI) is shown in Figure 5 C. The lines in Figure 5 B and 5 C are calculated least squares lines.
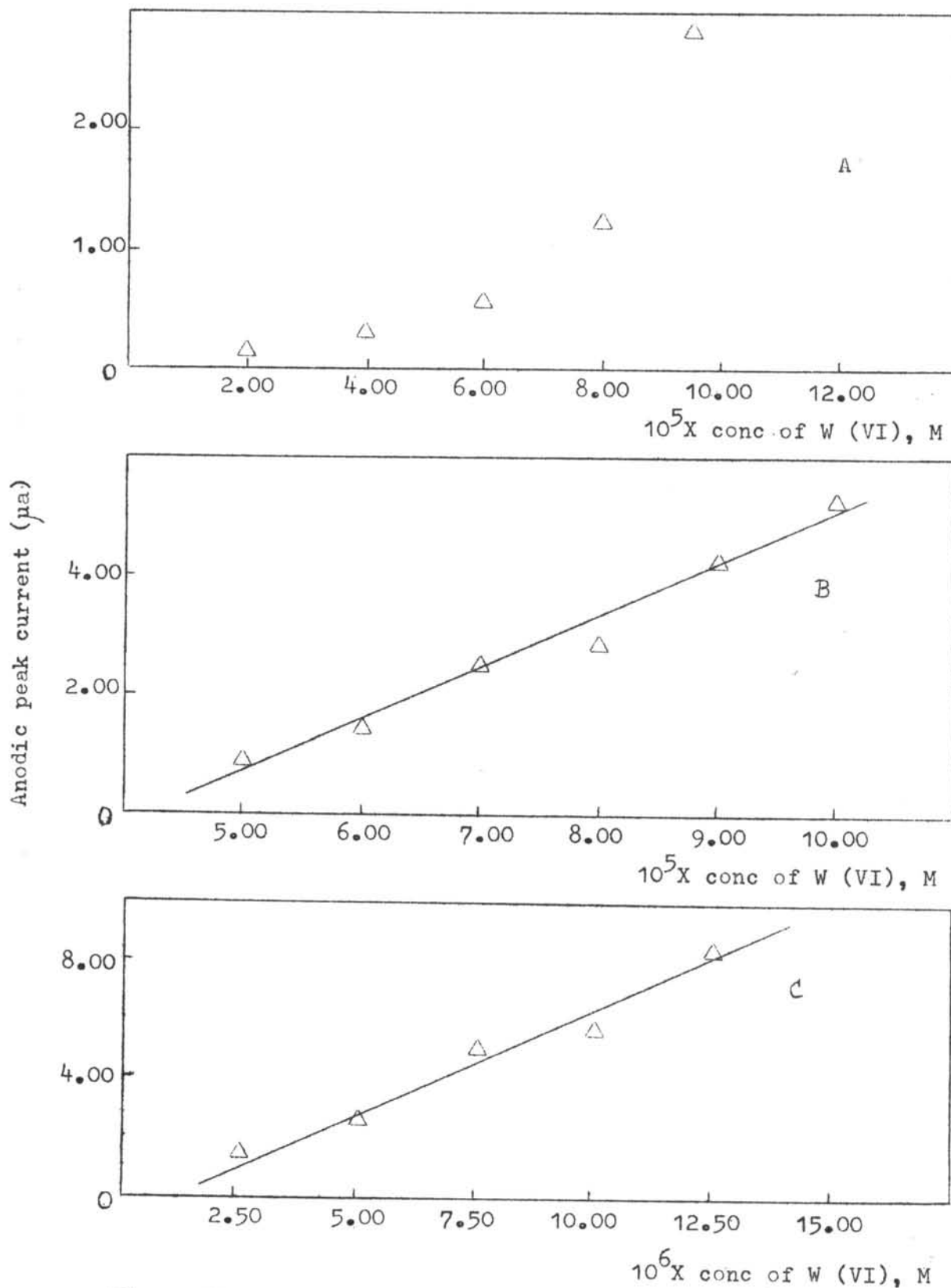
Figure 5 : The dependence of anodic peak current on concentration for anodic stripping analysis of W (VI) using electrodeposition time: A) 5 minutes, B) 10 minutes, and C) 20 minutes.