CHAPTER 5

ANODIC STRIPPING ANALYSIS OF VANADIUM

Polarographic determination of V (V) was investigated in the following supporting electrolytes: 0.1 M EDTA-0.1 M sodium acetate in the presence of molybdenum (22), NH_3 and NH_4Cl at the optimum pH of 10.1 (25°C) using N-anthranildiacetic acid for masking foreign cations (62), and H_3PO_4 - 0.06 M EDTA at pH 7 with 0.004% polyacrylamide as a maximum suppressor (63). The polarographic behavior of vanadyl ion in 0.4 - 2.0 M alkali nitrate solution at pH 5 (64), of V (V) in alkaline phosphate buffer pH 9.47 (65), and of V (IV) complexes with pyrocatechol and pyrogallol at pH 0 to 9 (66) were reported. Moreover, the reduction of V (V) and V (IV) to V (II) on a Hg electrode and Na or Zn amalgam electrode in 1 M H_2SO_4 and HCl was described (67).

Amperometric titration of vanadium with $CuSO_4$ solution containing 0.05% gelatin and 25% ethyl alcohol (68), with thiooxine in 2N acetic acid and sodium acetate buffer (pH 4.05), in 6N H_2SO_4 (69), in 0.5N H_2SO_4 (69), with 8-mercaptoquinoline in various acidic media (70), with ferrous ammonium sulfate solution (71), and with $K_2Cr_2O_7$ solution in 1-8N H_2SO_4 and H_2SO_4 - H_3PO_4 at 80°C (72) were described. In addition, potentiostatic coulometric determination of vanadium in vanadium-manganese mixture, in vanadium-iron mixture, and in the influence of chromium in process was possible by using K_2SO_4-acetate buffer of pH 4, or 2 M H_2SO_4 as supporting electrolyte (73).

Oscillopolarographic determination of vanadium was studied in 0.25 N ammonium oxalate (74), in 0.05 M EDTA-HCl (pH 0.6 - 3.2) in the presence of a 5-fold excess of Ti, Co, Cr, Fe, Ni, Cu, Mo, and W (74), in ammoniacal citrate at pH 7.0 to 9.0 (75), and in acetate and phosphate buffer solutions at pH 0 - 12 (76). In addition, vanadium in buffered soil solutions was possible to be determined in ammonium oxalate solution after extraction as the oxinate complex with $CHCl_3$ (76).

Voltammetric behavior of the V (V) - V (IV) system was investigated by using a Pt electrode in saturated K_2SO_4 - acetic acid buffer of pH 4.0 (77), in 5 X 10^{-5} M H_2SO_4 (77), and 2.0 M H_2SO_4 (77), and by using a rotating graphite electrode in H_2SO_4 (stronger than 12 N) (78), and in HCl (stronger than 6 N) (78). Moreover, voltammetric study of the VO^{2+}/V^{3+} couple at the platinized platinum electrode in perchloric acid was reported (79).

5.1 Evaluation of Electrolyte

5.1.1 0.2 M HCl - 0.2 M NH_4OH system at various pH

Since the stock solution of V (V) was prepared in HCl (see 2.1.3.3, p. 10), the use of HCl as supporting electrolyte was first tried. The pH of 1.00 X 10^{-4} M V (V) in 0.02 M HCl was found to be 2.3. This test solution gives no cathodic voltammetric peak. Thus, the effect of pH on the voltammogram of vanadium is studied. The higher pH (pH > 2.3) solution is prepared by the addition of 0.2 M NH_4OH and 0.2 M HCl to the stock solution.

In the system at pH 4, a cathodic peak of 5.00×10^{-4}M V (V) occurs at ca. -0.38 V. After electrodeposition of 1.00×10^{-4}M V (V) at -0.50 V for 10 minutes, an anodic peak is shown at +0.20 V. The cathodic and anodic voltammogram of vanadium are shown in Figure 6. The stripping voltammetric behavior of V (V) in various pH systems is listed in Table 8. The maximum anodic peak current is obtained from the system at pH 4.

5.1.2 0.2 M HCl - 0.2 M KOH system (pH 4 and 11)

To observe the effect of alkali salt on the stripping voltammogram of V (V), 0.2 M KOH is used instead of 0.2 M NH_4OH. Using 1.00×10^{-3}M V (V) in the system at pH 4 and pH 11, no cathodic voltammetric peak exhibits. However, the anodic stripping analysis of 1.00×10^{-3}M V (V) in either system is tried by electrodeposition at -0.50 V for 10 minutes and no anodic peak is obtained.

5.1.3 0.2 M H_2SO_4 - 0.2 M NH_4OH system at pH 4

The acid species is changed to 0.2 M H_2SO_4. The cathodic voltammogram of 1.00×10^{-3}M V (V) in 0.2 M H_2SO_4 - 0.2 M NH_4OH system at pH 4 shows a peak at potential ca. -0.43 V. After 5-minute-electrodeposition of 4.00×10^{-6}M V (V) at -0.50 V, an anodic peak is shown at +0.12 V. The anodic peak current obtained (15.54 μa) is lower than that in 0.2 M HCl - 0.2 M NH_4OH system (31.36 μa) at the same conditions.

Therefore, 0.2 M HCl - 0.2 M NH_4OH system at pH 4 is selected for the anodic stripping analysis of V (V) in this study.

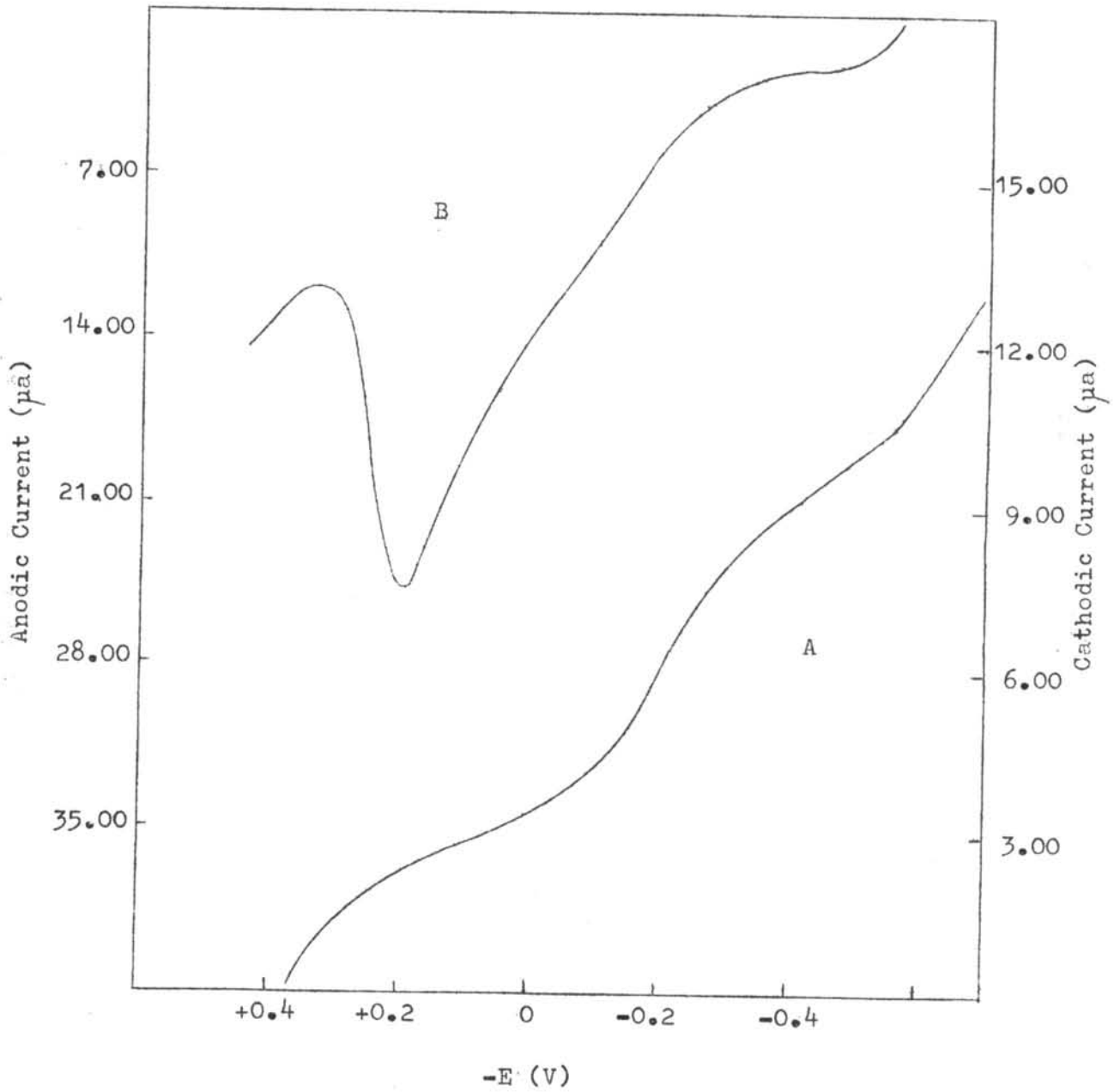

Figure 6 Voltammogram of vanadium in 0.2 M HCl-0.2 M NH_4OH system at pH 4; A) is the cathodic voltammogram of 5.00 X 10^{-4}M V (V), and B) is the anodic voltammogram after 10-minute-deposition of 1.00 X 10^{-4}M V (V).

Table 8 Effect of pH on the anodic stripping voltammogram of vanadium in 0.2 M HCl - 0.2 M NH_4OH system at pH 4.

pH 2	$i_{p,a}$ (μa)	$E_{p,a}$ (V)	Remark
2.3	none	none	no peak
4.0	12.56	+0.20	well-defined
4.2	8.44	+0.16	well-defined
6.1	2.66	+0.13	well-defined
7.0	none	none	no peak

5.2 Stripping Analysis

Electrodeposition of V (V) in 0.2 M HCl - 0.2 M NH_4OH system at pH 4 is performed at a constant potential of -0.50 V, corresponding to the potential of cathodic peak obtained at ca. -0.38 V. The time for electrodeposition of V (V) is varied as the concentration of V (V) in the test solution changed. The conditions for deposition of V (V) in 0.2 M HCl - 0.2 M NH_4OH system at pH 4, data for stripping analysis, and the detection limit are shown in Table 9. Using 5-minute-electrodeposition of 8.00×10^{-5} M - 4.00×10^{-4} M V (V), an anodic stripping peak exhibits at +0.16 V (Figure 7A) and the peak current obtained is directly proportional to the concentration of V (V) (see Figure 8A).

As the concentration of V (V) decreases to 6.00×10^{-5} M, two anodic peaks at ca. +0.07 V and ca. -0.10 V are shown in the stripping voltammogram after either 5-minute-electrodeposition or 10-minute-electrodeposition (see Figure 7B). These anodic peaks are overlapped and the peak currents are about the same in both cases.

In the concentration range of 6.00×10^{-6} M - 4.00×10^{-5} M and after 10-minute-electrodeposition, the anodic stripping voltammogram results two anodic peaks at ca. +0.33 V and ca. -0.14 V. However, the peak at ca. -0.14V is the predominant peak and the peak current at this potential is measured and shown in Table 9. The peak current obtained is linearly dependent on the concentration of V (V) (see Figure 8B).

Table 9 The conditions for electrodeposition of V (V) and data of anodic stripping analysis of vanadium in 0.2 M HCl - 0.2 M NH_4OH system at pH 4.

Deposition		Conc of V(V) (M)	$i_{p,a}^{a}$ (μa)	$E_{p,a}$ (V)	Detection limit (μa)
potential (V)	time (min)				
-0.50	5	4.00×10^{-4}	31.36 ± 0.42	+0.16	
		2.00×10^{-4}	21.73 ± 0.89		
		1.00×10^{-4}	11.81 ± 0.57		
		8.00×10^{-5}	7.36 ± 0.26		8.00×10^{-5}
-0.50	10	4.00×10^{-5}	1.87 ± 0.12	-0.14	
		3.00×10^{-5}	1.48 ± 0.07		
		2.00×10^{-5}	1.17 ± 0.05		
		1.00×10^{-5}	0.63 ± 0.05		
		8.00×10^{-6}	0.56 ± 0.03		
		6.00×10^{-6}	0.48 ± 0.02		6.00×10^{-6}
-0.50	20	6.00×10^{-6}	0.59 ± 0.01	-0.18	
		4.00×10^{-6}	0.49 ± 0.03		
		2.00×10^{-6}	0.38 ± 0.01		
		1.00×10^{-6}	0.28 ± 0.02		1.00×10^{-6}

[a] average peak current ± average deviation of more than 4 trials.

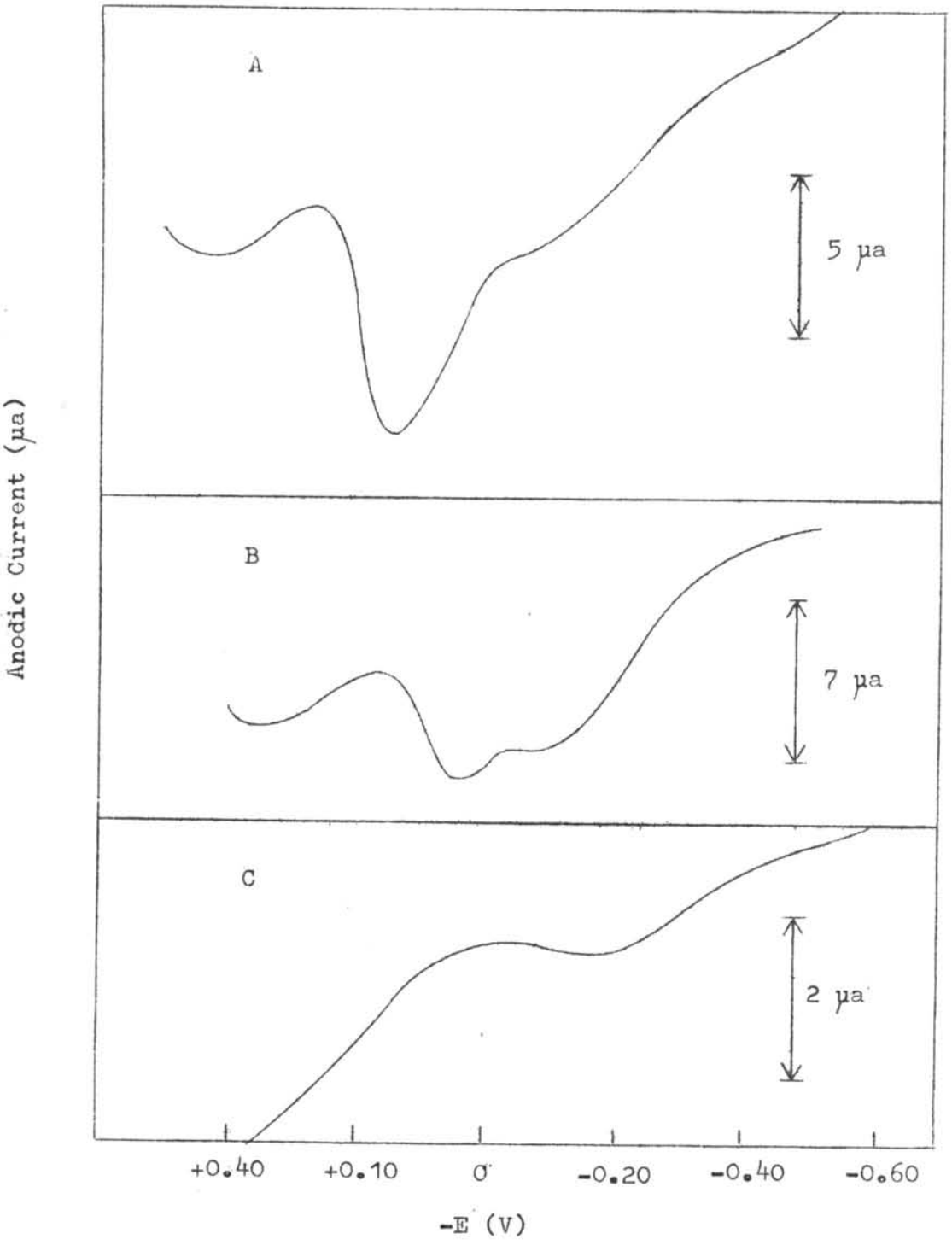

Figure 7 Anodic voltammogram of vanadium in 0.2 M HCl-0.2 M NH_4OH system at pH 4 after (A) 5-minute-deposition of 8.00×10^{-5} M V (V), (B) 10-minute-deposition of 6.00×10^{-5} M V (V), and (C) 20-minute-deposition of 6.00×10^{-6} M V(V).

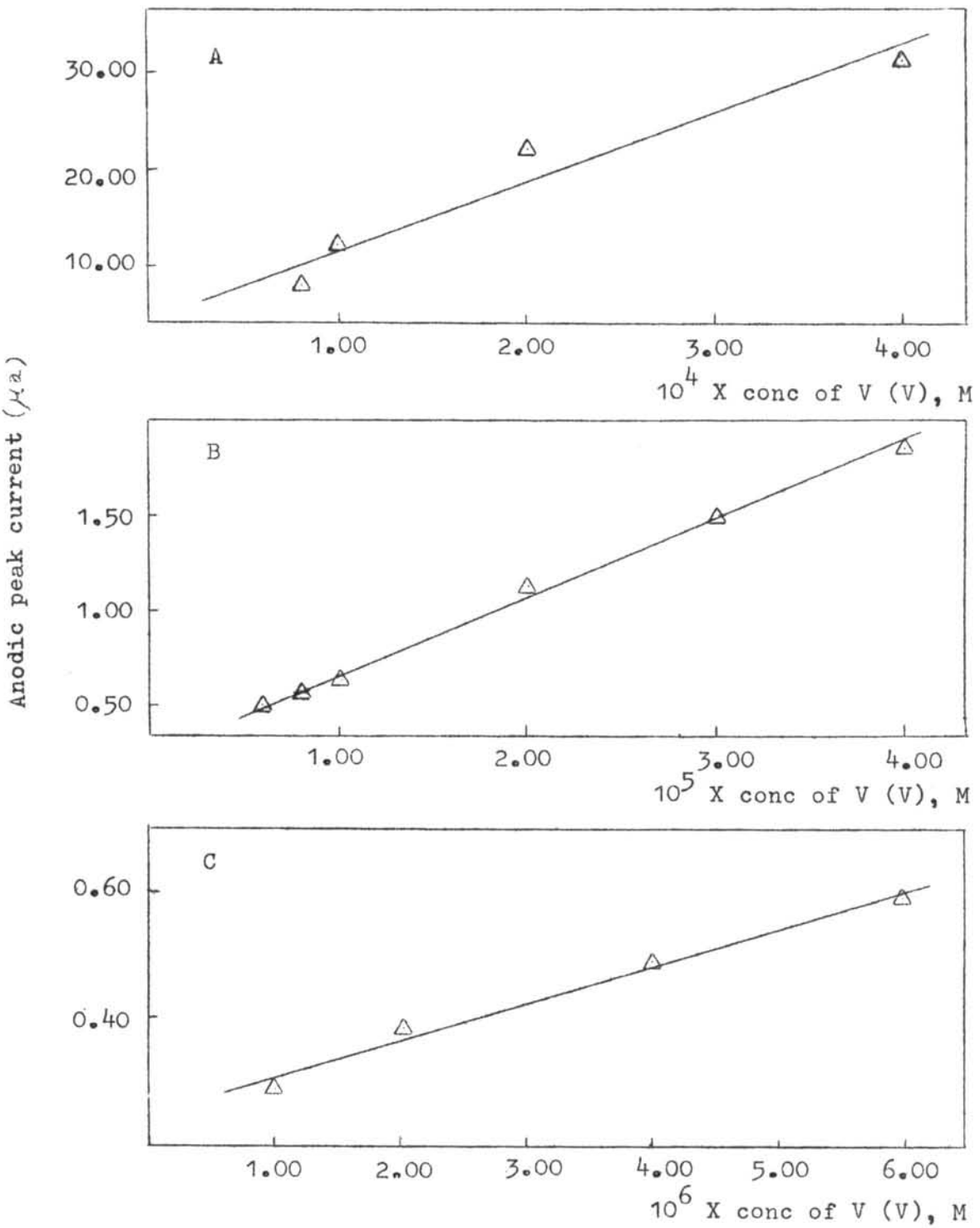

Figure 8 The linear dependence of anodic peak current on concentration for anodic stripping analysis of V (V) using electrodeposition time: A) 5 minutes, B) 10 minutes, and C) 20 minutes.

Finally, the 20-minute-electrodeposition of V (V) at the concentration lower than 6.00×10^{-6} M is studied. Only one anodic peak at -0.18 V is shown in the anodic stripping voltammogram and the anodic peak current is directly proportional to the concentration of V (V) (see Figure 8C). The lines in Figure 8 are calculated least squares lines.