

## CHAPTER 4

### ANODIC STRIPPING ANALYSIS OF ANTIMONY (III)

Polarographic behavior of antimony in the mixture solution of citrate and tartrate at pH 1-13 (30), in various pH solutions of mixture of 5-(methoxy-methyl)-8-hydroxyquinoline in 50% N,N-dimethyl formamide (31), and in strong phosphoric acid (16) had been investigated. The polarographic determination of antimony in the presence of Cu, Fe, Ga, Pb, In and Zn in 3 N HCl was possible and this method was used for determining  $10^{-3}$ - $10^{-4}$ % Sb in semiconductor alloys (32). Moreover the polarographic determination of  $10^{-10}$ - $10^{-8}$  g of Sb (III) in gallium arsenide, gallium and arsenic was claimed (33). Simultaneous polarographic determination of Sb (III) and Sn (IV) after coprecipitation with thorium hydroxide resulted 5% error (34). Polarograms of  $Sb_2O_3$  solutions in fused borax at a Ni electrode (35) and a Pt electrode (36) were studied. In addition, the effect of the following surfactants on the polarographic reduction of Sb (III) were reported: abietic acid (37), several terpenes and their derivatives (38), and poly (ethylene oxide) (39).


The pulse-polarographic behavior of antimony in various supporting electrolytes,  $HClO_4$ , 1 N  $H_2SO_4$ , 1, 3, 6, N HCl, 0.1 M acetate buffer (pH 4.7), 4 M HCl (neutral or pH 4), were examined

(40). Advantages of ac polarographic graphite method over dc polarography for the chloride complexes of Sb (III) were described (41). The electroreduction of Sb (III) in 1 M sulfuric acid + 0.01 M thiocyanate medium resulted a direct proportionality of current to concentration of Sb (III); the range of  $2 \times 10^{-5}$  -  $5 \times 10^{-4}$  M for the dc polarography and  $5 \times 10^{-6}$  -  $10^{-4}$  M for the ac method (42).

The oscillographic behavior of Sb (III) in nonbuffer solutions of indifferent electrolyte with pH 0-12.5 (43) and in 0.1-0.3 M trihydroxy-glutaric acid (44) were studied. Trace ( $10^{-4}\%$ ) of antimony in a 5 g manufacturing  $\text{Na}_2\text{S}_2\text{O}_4$  sample was determined by oscillographic polarography (45). The concentration of more than  $4 \times 10^{-8}$  M antimony was possible to determine in 0.2 M HCl by the differential oscillographic polarography (46). In addition, the oscillographic behavior of the complex of antimony (III) and ferron was described (47).

The anodic voltammetric characteristic of antimony in 0.1 N NaCl, 0.1 N NaF, 0.1 N  $\text{NH}_4\text{Cl}$  + 0.1 N  $\text{NH}_4\text{OH}$ , 0.1 N  $\text{Na}_2\text{C}_2\text{O}_4$ , 0.25 N HCl, 0.1 N acetic acid + 0.1 N sodium acetate and 0.1 N sodium acetate were studied (48). Using anodic stripping voltammetry, a more accurate formula for calculating the number of the electrons participating in anodic process of Sb was proposed (49). An equation was developed to describe the effect of temperature variations on the height of the anodic peak for the stripping





analysis of Sb (III) in 0.2 N  $\text{NH}_4\text{NO}_3$  in ethanol (50). Moreover the behavior of antimony during stripping analysis was studied in 1 M sodium carbonate + 0.25 N sodium hydrogen tartrate by using hanging Hg drop (51). The method of anodic stripping voltammetry for determination of trace amounts of antimony in natural water (52), and in Zn,  $\text{ZnS}$  and  $\text{ZnSe}$  (53) had been illustrated. The determination of antimony in sulfide-alkaline solution (54) and in 2 N KOH solution (55) were reported. The picogram range of antimony could be determined by using rotating carbon paste electrode (56). In addition, the application of anodic potential-step stripping voltammetry for the determination of Sb (III) in 1 M  $\text{H}_2\text{SO}_4$  + 0.01 M KSCN was investigated; calibration curve of Sb (III) was found to be linear in the range of 0.01 - 0.1 ppm by analysis at time  $t = 1.25$  seconds on current-time curve (57).

In the present chapter, conditions for anodic stripping analysis of Sb (III) as well as the sensitivity and detection limit of Sb (III) are demonstrated.

#### 4.1 Evaluation of Electrolyte

Since the electrolyte chosen, HCl, gave a well-defined cathodic voltammogram and a well-defined stripping voltammogram of antimony, no other electrolyte was tried. However, the

sensitivity of Sb (III) in different concentration of HCl was checked. The cathodic voltammogram of Sb (III) shows a peak at ca. -0.40 V in 0.1, 0.5, 1.0 and 2.0 M HCl. These cathodic peak currents are nearly the same value. In stripping voltammetry, an anodic peak of antimony in the mentioned concentration of HCl is shown at ca. 0V. The anodic peak current is higher in either 1.0 M or 2.0 M HCl. Thus, for economy 1.0 M HCl was selected as supporting electrolyte for stripping analysis of Sb (III). The cathodic voltammogram and anodic voltammogram of antimony in 1.0 M HCl are shown in Figure 3.

#### 4.2 Stripping Analysis

The potential of -0.40 V is used for electrodeposition of Sb (III) in 1.0 M HCl because of its cathodic peak at ca. -0.40 V. The deposition time is varied owing to the concentration of Sb (III) in the working solution. The conditions for electrodeposition of Sb (III) in 1.0 M HCl, data of stripping analysis and the detection limit are listed in Table 4. In each condition, the linear dependence of anodic peak current on concentration of Sb (III) is obtained (see Figure 4). The lines in Figure 4 are calculated least squares lines.



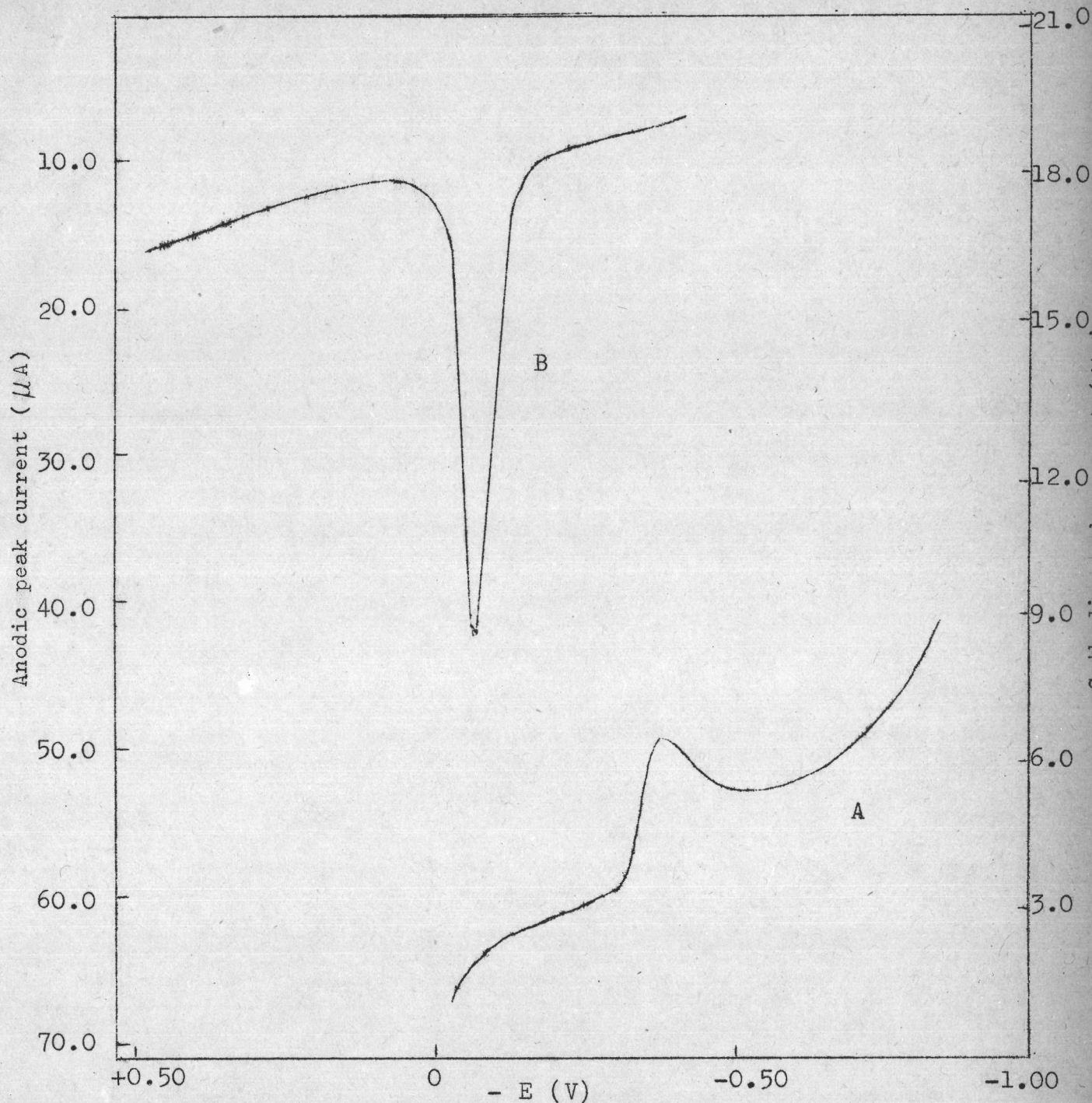


Figure 3 Voltammograms of Sb(III) in 1 M HCl; A is the cathodic voltammogram of Sb(III) in  $4.95 \times 10^{-5} \text{ M}$  and B is the anodic voltammogram of antimony after deposition of  $5.94 \times 10^{-6} \text{ M}$  Sb(III) for 10 min.

Table 4 Conditions for deposition of Sb (III) and data  
of stripping analysis of antimony in 1 M HCl

Deposition		Conc. of Sb (III) (M)	$i_{p,a}^a$ ( $\mu A$ )	detection limit (M)
Potential (V)	time (min)			
-0.40	3	$9.90 \times 10^{-5}$	$142.64 \pm 13.63$	$9.90 \times 10^{-6}$
		$7.92 \times 10^{-5}$	$115.57 \pm 10.78$	
		$5.94 \times 10^{-5}$	$90.43 \pm 10.83$	
		$3.96 \times 10^{-5}$	$62.08 \pm 4.38$	
		$1.98 \times 10^{-5}$	$36.12 \pm 4.86$	
		$9.90 \times 10^{-6}$	$22.01 \pm 3.06$	
-0.40	10	$9.90 \times 10^{-6}$	$94.06 \pm 2.59$	$9.90 \times 10^{-7}$
		$7.92 \times 10^{-6}$	$44.71 \pm 5.76$	
		$5.94 \times 10^{-6}$	$32.15 \pm 2.52$	
		$3.96 \times 10^{-6}$	$22.63 \pm 1.97$	
		$1.98 \times 10^{-6}$	$10.40 \pm 1.11$	
		$9.90 \times 10^{-7}$	$3.70 \pm 0.32$	
-0.40	20	$9.90 \times 10^{-7}$	$0.98 \pm 0.07$	$1.98 \times 10^{-7}$
		$7.92 \times 10^{-7}$	$0.83 \pm 0.04$	
		$5.94 \times 10^{-7}$	$0.66 \pm 0.06$	
		$3.96 \times 10^{-7}$	$0.53 \pm 0.04$	
		$1.98 \times 10^{-7}$	$0.32 \pm 0.03$	

a

average peak current  $\pm$  average deviation of more than 4 trials



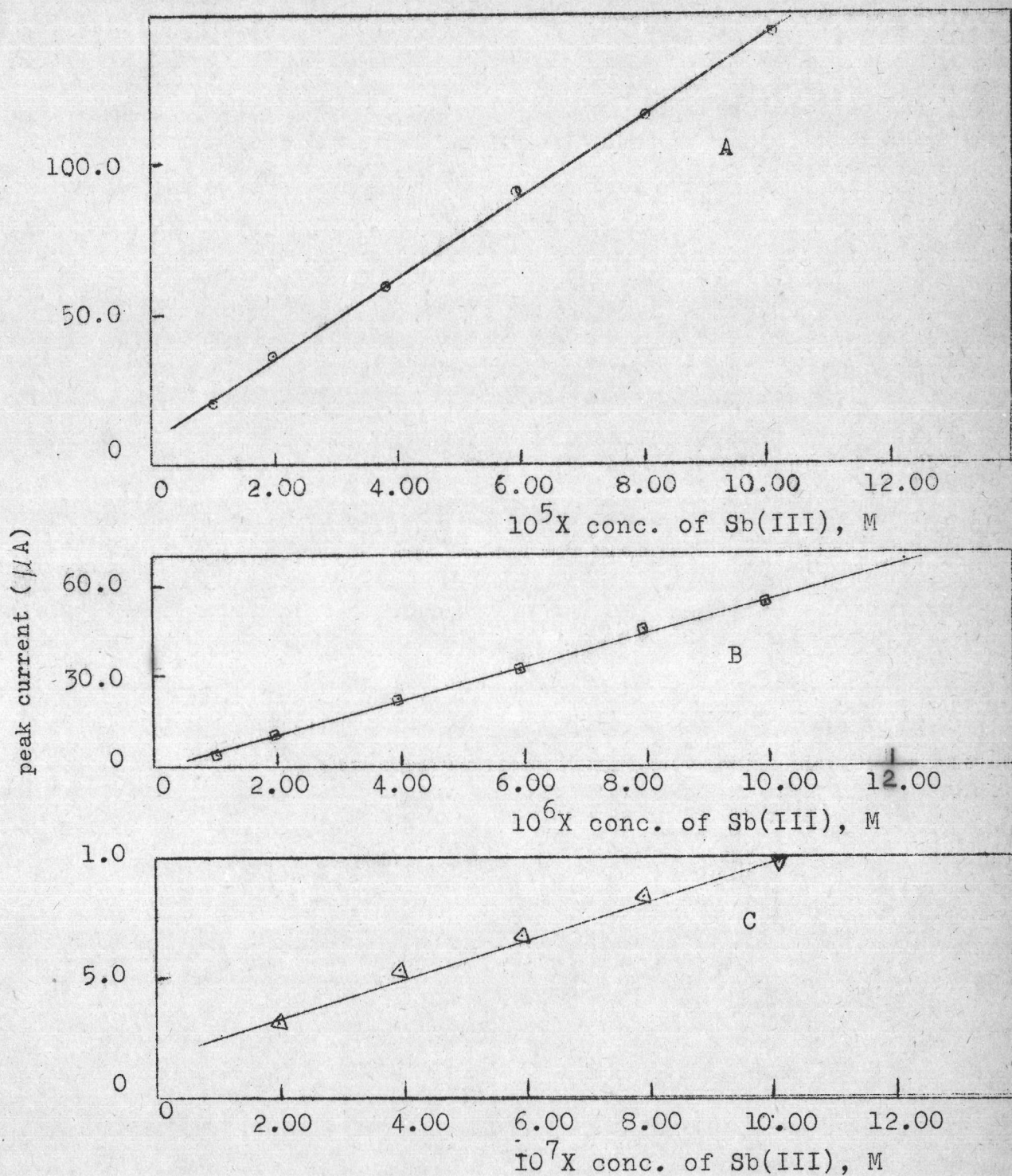


Figure 4 The linear dependence of anodic peak current on concentration for anodic stripping analysis of Sb(III) using electrodeposition time: A) 3 min, B) 10 min and C) 20 min.