

CHAPTER 6

ANODIC STRIPPING ANALYSIS OF TIN (IV)

The polarographic reduction of Sn (II) in molten ammonium sulfamate at 435°K (73), in aqueous molten $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$, $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (63), as well as in HClO_4 , H_2SO_4 and acetic acid in some surface active agents (several terpenes and their derivatives) (38) had been studied. The determination of Sn (II) by both dc and ac polarography was reported in 5-40% HF (65) and in $\leq 50\%$ HF (74) supporting electrolyte.

Tin (IV) in Cd-Sn-As semiconductor compound could be determined by ac polarographic method (75) as well as in heat resistant alloys was determined by vector, oscillographic and electronic technique (23). Moreover, tin in SnCl_2 was determined in 0.8 M tartaric acid and 2.5 M HCl by oscillographic analysis (76). The dc and ac voltammetric peak height of Sn (IV) in 2.4 N HCl was enhanced by addition of cation-active surfactants (77). On addition of surface active materials, oscillogram of both tin and Sn-Cu mixture changed shapes (78). The oscillographic behavior of surface active complexes of Sn (IV) with ferron in 0.5 M NaNO_3 and acetate buffer solutions were reported (47).

The kinetic of Sn deposition on rotating Sn electrode from 0.25 M SnSO_4 in 1 M H_2SO_4 (79), pulse polarographic behavior of Sn in 6 N HCl (40), and vector polarographic with anodic stripping analysis of Sn in Ga, As, GaAs and GaP (33, 80) had been investigated.

Polarographic characteristics of the anodic peak of tin in 0.1 N NaCl, 0.1 N NaF, 0.1 N NH_4Cl + 0.1 N NH_4OH , 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). By conventional dc, conventional ac, rapid dc, rapid ac, inverse dc and inverse ac polarographic method, the determination of tin (IV) (81) and tin in geological samples (82) in HCl supporting electrolyte were resulted. In addition, inverse voltammetric determination of tin and lead in ^{the} presence of each other at the carbon-paste electrode was reported (83). Trace of tin (II) and tin (IV) in different solvent (water, methanol) (84) as well as tin (II) in 1 M HCl (57) had been investigated by anodic stripping voltammetry (84). Moreover, the determination of tin in seawater and other marine samples were done by using anodic stripping voltammetry with in situ mercury deposition on a polish glassy carbon electrode (85).

The conditions for anodic stripping analysis, sensitivity and detection limit of Sn (IV) are reported in this chapter.

6.1 Evaluation of Electrolyte

The determination of tin by polarography or anodic stripping voltammetry is complicated by the strong tendency of tin (IV) species to hydrolyse and polymerise. For this reason a hydrochloric acid (1 to 7 M) supporting electrolyte is usually chosen to suppress hydrolysis and stabilize tin as a chloro complex ion (86). Cathodic voltammograms of Sn (IV) are attempted in 0.1 M KNO_3 , 0.1 M NaCl, 0.5 M, 2.0 M HNO_3 and 1 M HCl. No cathodic peak is observed in 0.1 M KNO_3 and 0.1 M NaCl. A well-defined cathodic peak is shown in 0.5 M, 2.0 M HNO_3 and 1 M HCl. By stripping analysis of Sn (IV) in the above electrolytes, A well-defined anodic peak is obtained only in 1 M HCl. For this reason, 1 M HCl is chosen as the supporting electrolyte for the anodic stripping analysis of Sn (IV). The cathodic and anodic voltammograms of tin are shown in Figure 7. The cathodic voltammetric peak of Sn (IV) shows at ca.-0.70 V and the anodic voltammetric peak is at ca.-0.50 V.

6.2 Stripping analysis

The cathodic peak potential of Sn (IV) in 1.0 M HCl occurs at ca.-0.70 V, therefore the potential of -0.80 V is chosen for the electrodeposition of Sn (IV). For checking

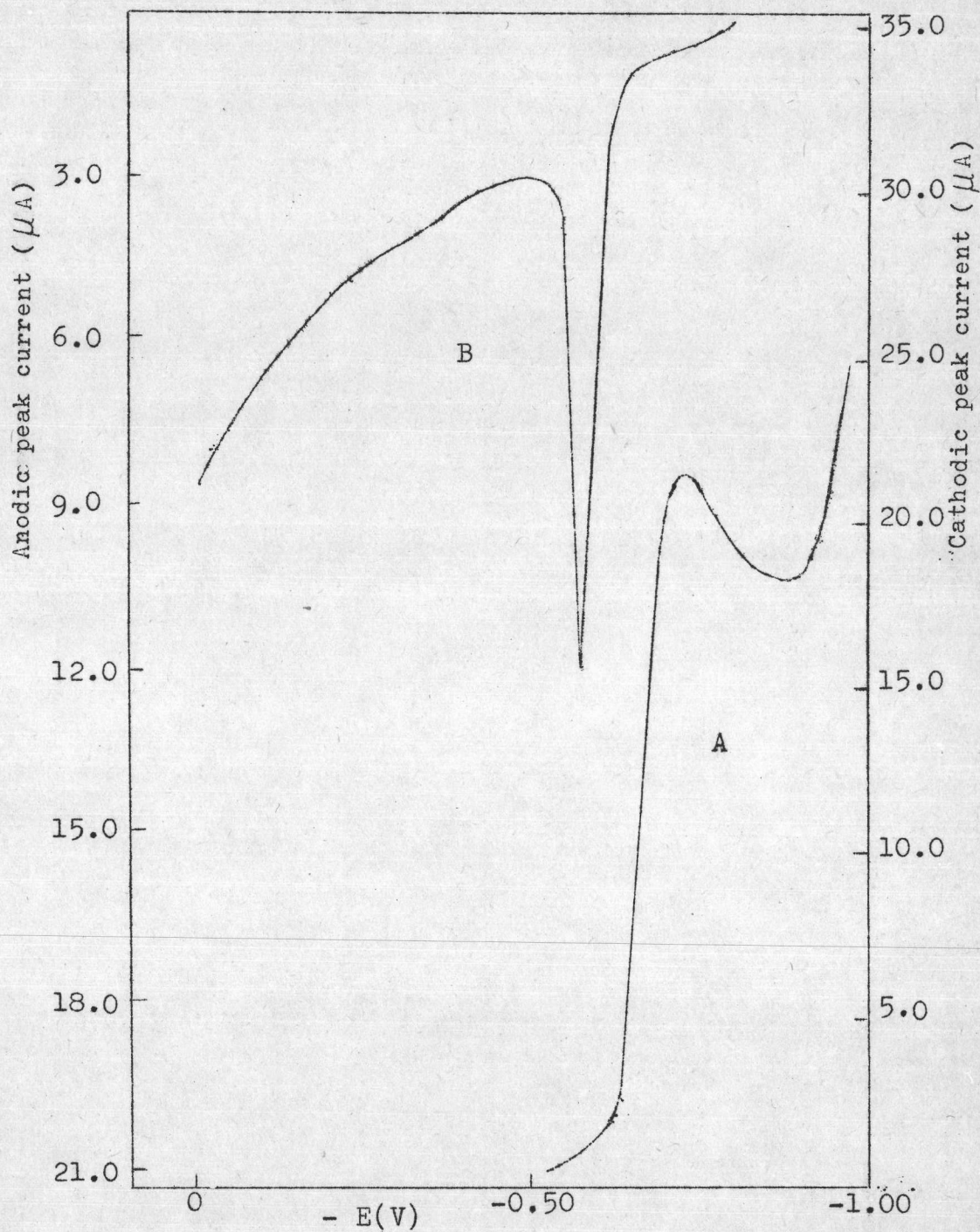


Figure 7 Voltammograms of tin in 1.0 M HCl; A is the cathodic voltammogram of $9.32 \times 10^{-5} M$ Sn(IV) and B is the anodic voltammogram of tin after deposition of $9.32 \times 10^{-6} M$ Sn(IV) for 15 min.

sensitivity of Sn (IV) by this method, the concentration of Sn (IV) in the working solution is varied, and the time for the electrodeposition of Sn (IV) is simultaneously varied. Conditions for electrodeposition of Sn (IV) in 1.0 M HCl, data of stripping analysis, and the detection limit are given in Table 6. In each condition, the linear dependence of anodic peak current on concentration of Sn (IV) is obtained (see Figure 8). The lines in this figure are calculated least square lines.

Table 6 Conditions for deposition of tin (IV) and data of stripping analysis of tin in 1 M HCl

Deposition		Conc. of Tin (IV) (M)	^a $i_{p,a}$ μA	Detection limit (M)
Potential (V)	time (min)			
-0.80	4	1.86×10^{-4}	138.55 ± 11.75	1.86×10^{-5}
		9.32×10^{-5}	63.00 ± 1.60	
		7.46×10^{-5}	46.88 ± 5.03	
		5.59×10^{-5}	30.30 ± 1.45	
		3.73×10^{-5}	16.68 ± 1.86	
		1.86×10^{-5}	1.22 ± 0.09	
-0.80	15	1.86×10^{-5}	24.28 ± 0.77	1.86×10^{-6}
		9.32×10^{-6}	10.99 ± 0.79	
		7.46×10^{-6}	8.16 ± 0.74	
		5.59×10^{-6}	5.74 ± 0.56	
		3.73×10^{-6}	2.91 ± 0.20	
		1.86×10^{-6}	0.93 ± 0.10	

^a
average anodic peak current \pm average deviation of more than
4 trials.

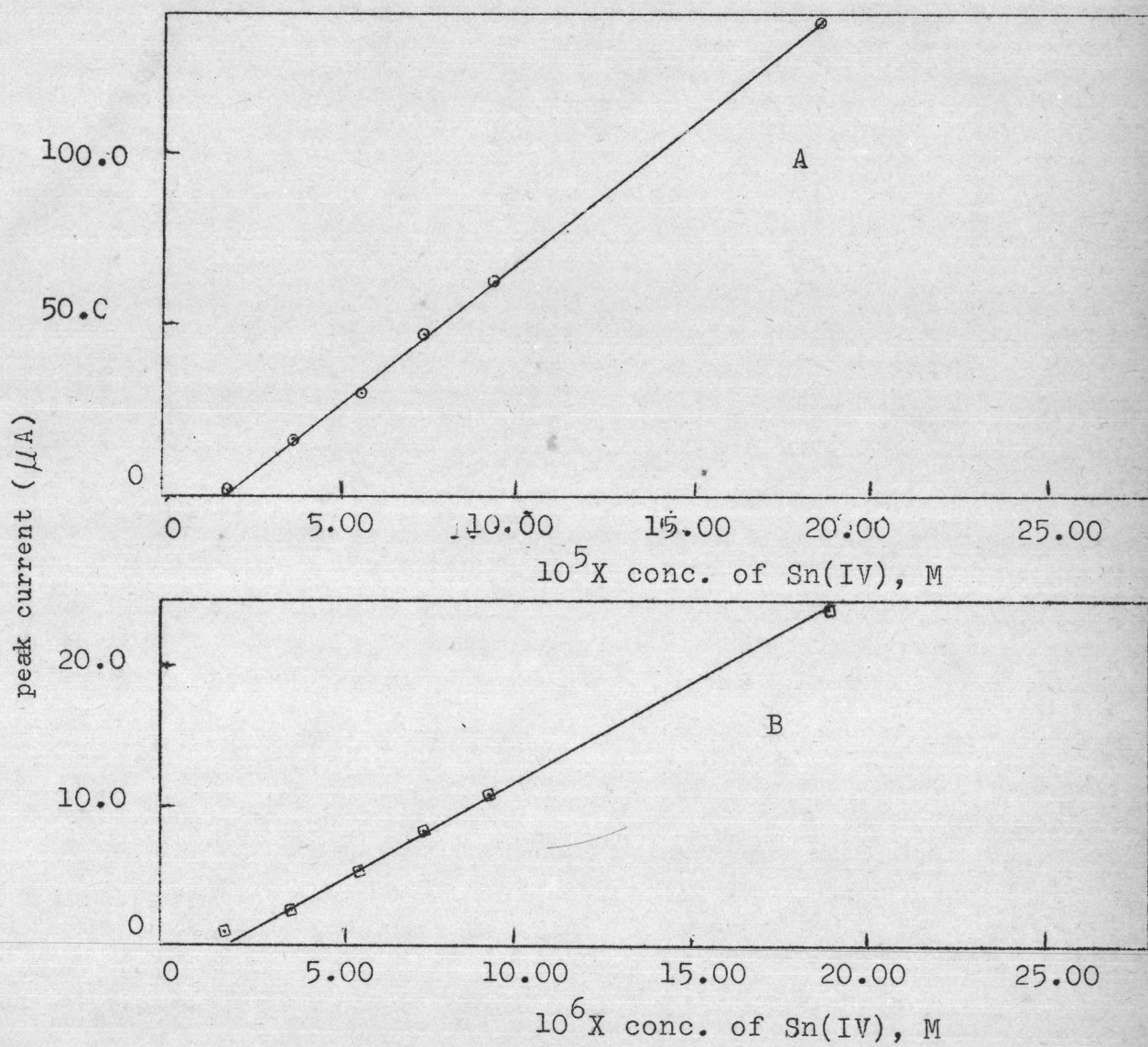


Figure 8 The linear dependence of anodic peak current on concentration for anodic stripping analysis of Sn(IV) using electrodeposition time: A) 4 min. and B) 15 min.