CHAPTER 5

ANODIC STRIPPING ANALYSIS OF BISMUTH (III)

Polarographic behavior of bismuth in the following electrolyte had been investigated; in strong phosphoric acid (16), pH 0-2 of perchloric acid (58), pH 1-13 of citrate and tartrate (30), 5-(methoxymethyl)-8-hydroxyquinoline in 50% N,N'-dimethyl formamide (31, 59), as well as in 0.1 M succinic acid at about pH 3 in the presence of 0.005% gelatin (60). The effects of some surfactants; abietic acid in 1 N HCl, H_2SO_4, $HClO_4$, NaOH and formic acid (37), terpenes and their derivatives in 1 N HCl, $HClO_4$, H_2SO_4, and formic acid (38), and camphor in 2 N $HClO_4$(61), on the polarographic reduction of bismuth were reported. The limiting currents for the reduction of Bi (III) in fused $Ca(NO_3)_2 \cdot 4 H_2O$ with a Pt microelectrode and a rotating disk electrode were examined (62). In addition, the polarographic behavior of Bi (III) in the aqueous molten salt of $Ca(NO_3)_2 \cdot 4H_2O$, $Ca(NO_3)_2 \cdot 4 D_2O$, $LiNO_3 \cdot 3 H_2O$ and $CaCl_2 \cdot 6 H_2O$ were described (63).

The determination of bismuth in the presence of great amounts of antimony by dc polarography (64), in 5-40% HF solutions by dc and ac polarography (65), in the presence of a large excess of rare earths by ac polarography (66), and in the pharmaceutical

dosage forms by dc polarography (67) had been discussed. Moreover, bismuth in the binary mixtures of Bi and Ag, Fe, Hg or Au could be analyzed by an indirect ac polarography (68).

The oscillopolarographic characteristics of Bi (III) in the optimum pH 2-4 of 0.1-0.3 M trihydroxyglutaric acid (44) as well as the complexes of Bi (III) with ferron in 0.5 M $NaNO_3$ and acetate buffer solutions at pH 2-7 (47) were reported. The trace (10^{-4}%) of bismuth could be determined in sodium dithionite by oscillographic polarography (45).

Anodic voltammetric analysis of bismuth in gallium arsenide, gallium and arsenic in 2 N KOH supporting electrolyte resulted a detection range of 10^{-10}- 10^{-8}g (33). Anodic stripping analysis of bismuth in 0.1 N NaCl, 0.1 N NaF, 0.1 N NH_4Cl + 0.1 N NH_4OH, 0.1 N $Na_2C_2O_4$, 0.1 N acetic acid + 0.1 N sodium acetate and 0.1 N sodium acetate (48), in 1 M H_2SO_4(57), as well as in 0.25 N HCl (48, 69) were reported. The determination of bismuth in nanogram amounts (52) and in the range of 10^{-6}- 10^{-7}% Bi (70) were done by anodic stripping technique. Moreover, trace of bismuth in Zn, ZnS and ZnSe in the following supporting electrolyte: 0.01, 0.05, 0.25 and 1 N HCl, 0.1 N NaCl and 0.1 N NH_4F (53) as well as the small amount of Bi (III) down to 10^{-7}M in the presence of 10^4times as much Pb (71) could be determined by anodic stripping method. In addition, anodic stripping voltammetry with a polished glassy carbon electrode mercury plated in

situ was used for the determination of bismuth in seawater and a variety of marine organisms (72).

In this chapter, the HNO_3 serves as the supporting electrolyte for study Bi (III). The anodic stripping analysis conditions, sensitivity and detection limit of Bi (III) are described.

5.1 Evalution of Electrolyte

Owing to the decomposition of $BiCl_3$ to BiOCl in dilute HCl, HNO_3 and H_2SO_4, $Bi(NO_3)_3$ was chosen for this study. Bismuth nitrate is very soluble in HNO_3 and amperometric titration of bismuth is done in the pH 1-2 (10,11). Thus Bi (III) in the concentration of nitric acid from 0.5 M to 0.06 M, giving the pH of 0.3 to 1.5, was examined. The voltammogram of Bi (III) in 0.5 - 0.06 M HNO_3 shows a cathodic peak at ca.-0.20 V. The stripping voltammogram of bismuth in 0.5 - 0.06 M HNO_3 yields an anodic peak at about 0 V. In addition, the anodic peak current obtained in each case is about the same volue. This can be concluded that the concentration of HNO_3 in the range of 0.5 - 0.06 M has no effect on the stripping current of bismuth. Therefore, 0.5 - 0.06 M HNO_3 is used as supporting electrolyte for this anodic stripping analysis of Bi (III). However, most stripping currents recorded in this experiment were obtained from 0.5 M HNO_3.

The cathodic and anodic voltammogram of Bi (III) in 0.5 M HNO_3 are shown in Figure 5.

5.2 Stripping Analysis

Corresponding to the cathodic peak of Bi (III) at ca.-0.20 V, the potential of -0.20 V is set for the electrodeposition of Bi (III) in 0.5 M and 0.06 M HNO_3. Conditions for the anodic stripping analysis of Bi (III) in each concentration range is indifferent except the time for deposition. Data, conditions and detection limit for anodic stripping analysis are given in Table 5. In each conditions, the anodic peak current is directly proportional to the concentration of Bi (III) (see Figure 6). The lines in this figure are calculated least squares lines.

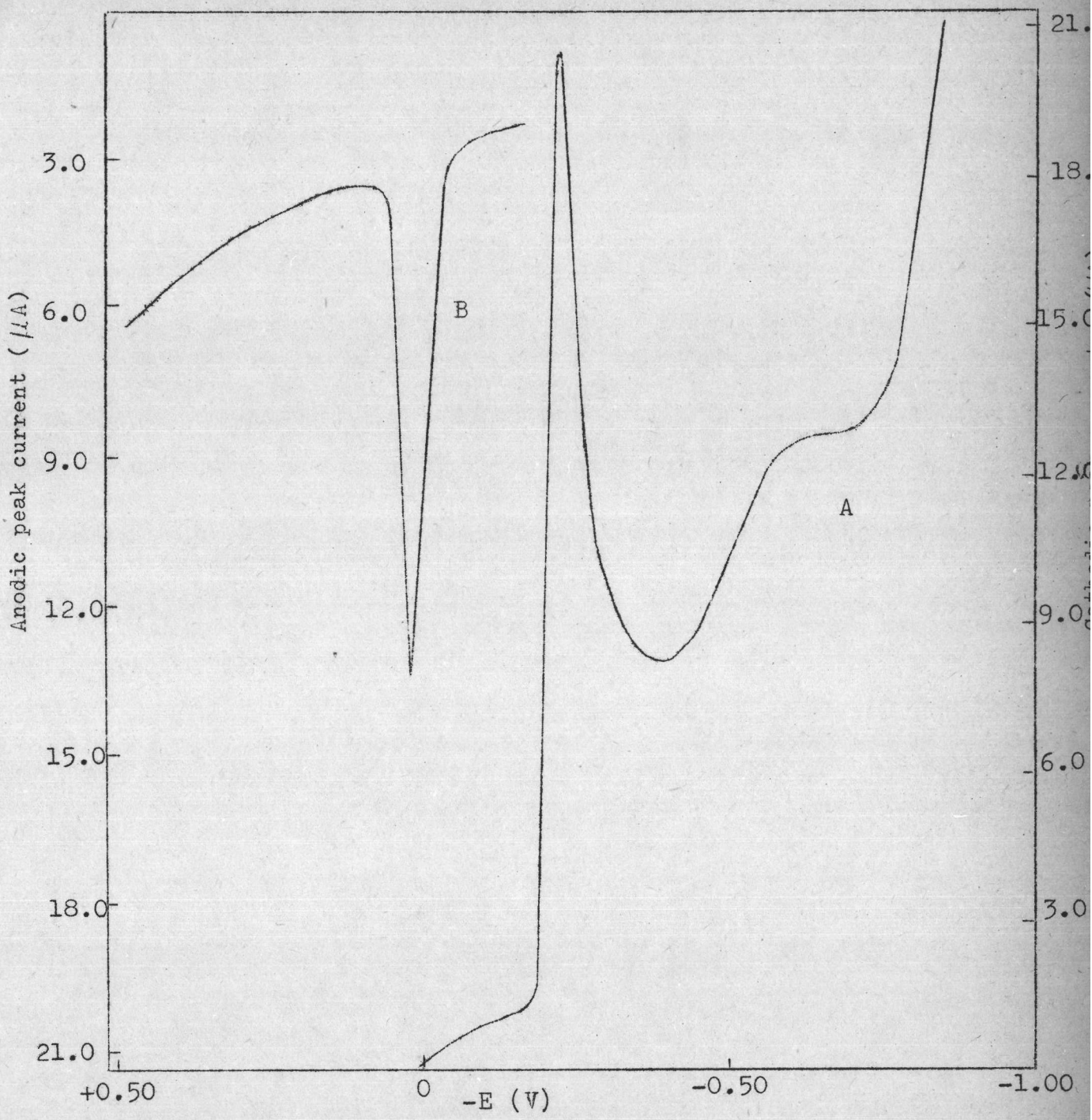

Figure 5 Voltammograms of bismuth in 0.5 M HNO_3; A is the cathodi voltammogram of $3.85X10^{-6}$M Bi(III) and B is the anodic voltammogram of bismuth after deposition of $2.50X10^{-6}$M Bi(III) for 10 min.

Table 5 Conditions for the deposition of Bi (III) and data of stripping analysis of bismuth in 0.06 and 0.5 M HNO_3

Deposition		Conc.of Bi (III)	$i^a_{p,a}$	Detection limit
Potential (V)	time (min)	(M)	(μA)	(M)
-0.20	10	2.50×10^{-5}	147.93 ± 20.27	
		1.00×10^{-5}	57.49 ± 6.72	
		9.00×10^{-6}	51.07 ± 3.97	
		8.00×10^{-6}	44.87 ± 2.77	
		7.00×10^{-6}	38.70 ± 1.49	
		6.00×10^{-6}	30.64 ± 2.46	
		5.00×10^{-6}	25.33 ± 1.06	
		4.00×10^{-6}	17.75 ± 2.07	
		3.00×10^{-6}	11.49 ± 0.79	
		2.50×10^{-6}	10.73 ± 1.15	
		2.00×10^{-6}	8.52 ± 0.40	
		1.00×10^{-6}	0.70 ± 0.12	1.00×10^{-6}
-0.20	20	1.00×10^{-6}	2.33 ± 0.26	
		9.00×10^{-7}	2.07 ± 0.20	
		8.00×10^{-7}	1.76 ± 0.20	
		6.00×10^{-7}	1.16 ± 0.07	
		4.00×10^{-7}	0.58 ± 0.06	
		2.00×10^{-7}	0.07 ± 0.01	2.00×10^{-7}

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

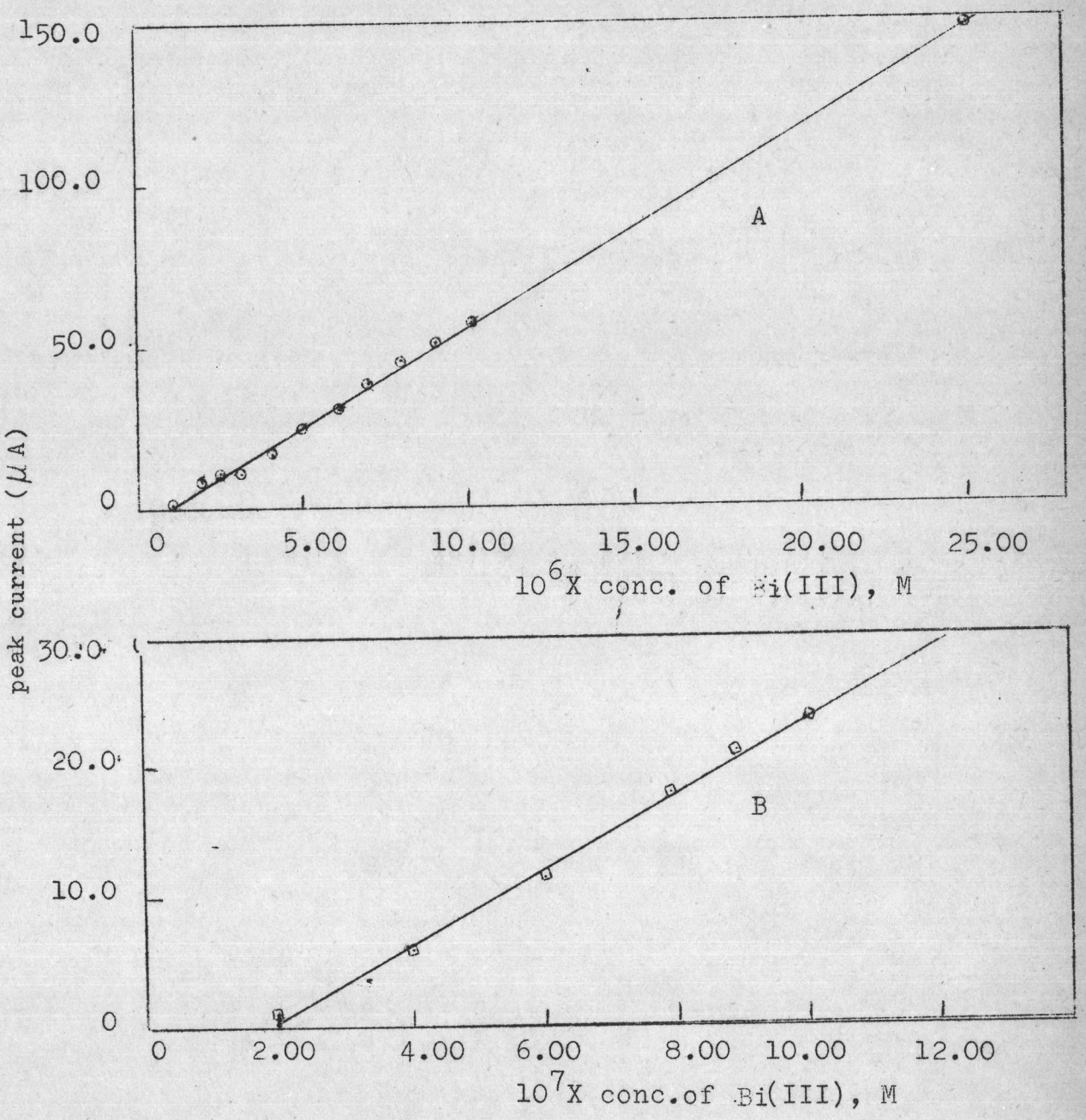

Figure 6 The linear dependence of anodic peak current on concentration for anodic stripping analysis of Bi(III) using electrodeposition time: A) 10 min and B) 20 min.