



## CHAPTER 3

### ANODIC STRIPPING ANALYSIS OF ARSENIC (III)

The literature on the polarographic reduction of arsenic in various media was reviewed in reference 12. The mechanism of polarographic reduction of As (III) in organic acids (acetic, oxalic, tartaric, lactic, citric, succinic acid and citrate-phosphate buffer solutions) (13), in weakly acid unbuffered solutions ( $\text{HClO}_4$ - $\text{NaClO}_4$  and  $\text{H}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$  at ionic strength 0.1)(14), in  $\text{NH}_3$  solution with the presence of 0.005% gelatin (15) and in strong phosphoric acid (16) had been investigated. The effects of organic surfactants on polarographic reduction of As (III) in 1 N  $\text{H}_2\text{SO}_4$ , HF and HCl were studied (17). Direct pulse polarographic determination of As (III) in water and aqueous extracts of garbage dumps in 2 M  $\text{H}_2\text{SO}_4$  and 2 M NaCl had been reported with a detection limit of 20 ppb of As (III)(18). Using superimposed sinusoidal voltage and a high Hg drop rate, polarographic reduction of molybdoarsenate in 1 M  $\text{NaClO}_4$ -0.5 mM  $\text{Na}_2\text{MoO}_4$ -0.057 M  $\text{HClO}_4$  in 10% methyl ethyl ketone gave a detection limit of 0.7  $\mu\text{M}$  As (19). In addition, reduction of molybdoarsenate in 1 M  $\text{NaClO}_4$ -0.5 mM  $\text{Na}_2\text{MoO}_4$ -0.3 M  $\text{HClO}_4$  in 50% methyl ethyl ketone by using superimposed sinusoidal voltage and a natural low Hg drop rate resulted in 2.

detection limit of  $10^{-7}$ M (20). The oscillopolarograms of As (III) in  $(\text{NH}_4)_2\text{SO}_4$ , LiCl, HCl were examined (21) and the optimum conditions for obtaining a well-defined oscillopolarogram of As (III) in 0.008 - 0.1 N  $(\text{NH}_4)_2\text{SO}_4$  (20) and in 0.004 N  $(\text{NH}_4)_2\text{SO}_4$  (22) were reported. Moreover, the reproducibility and sensitivity of oscillopolarographic determination of arsenic in heat-resistant alloys were illustrated (23). Arsenic in Te, Se, and metals forming solution ammine complexes was polarographically determined in the supporting electrolyte containing 0.08 - 0.12 M HI, 63 - 72 mM Fe (III); and 26 - 30 mM ascorbic acid (24). Recently, differential pulse polarography of As (III) in a number of supporting electrolytes were studied and 1 M HCl was found to give the greatest sensitivity; the detection limit is ca.  $4 \times 10^{-9}$ M (25).

Anodic stripping analyses of As (III) in some supporting electrolytes at a Pt electrode were investigated and 1.0 N HCl was found to be the most suitable medium with the sensitivity of  $2.00 \times 10^{-7}$ M As; the anodic peak current is linearly related to the time of electrolysis in the range 1 - 20 minutes (26). The determination of less than  $2.00 \times 10^{-7}$ M As (III) in 1 N HCl by the method of addition, using inverse voltammetry with amalgam accumulation was described (27). Kaplin and his coworkers had studied anodic stripping analysis of As on graphite, Pt and Au electrode and the sensitivity of As determination on a graphite electrode was reported as  $10^{-7}$  g/cm<sup>2</sup> when Cu, Au, Pd or Pt ions

were simultaneously electrodeposited (28). In addition, anodic stripping analysis of As (III) by codeposition with Cu (II) in 0.24 M HCl and stripping out in 4 M HCl was claimed with a relative deviation of more than 10% for determining 1-20  $\mu\text{g As/cm}^3$  (29).

In this chapter the conditions for anodic stripping analysis of As (III) in various electrolytes are described. The optimum conditions for stripping analysis and the sensitivity of As (III) in the electrolyte chosen is reported.

### 3.1 Evaluation of Electrolyte

Cathodic voltammograms of As (III) in the following supporting electrolytes are tried and no voltammetric peak is observed; 0.1 M HCl and 2 M sodium acetate buffer solution, pH 1.15, 2.5, 3.7, 5.05 and 8.65 of 0.1 M HCl and 0.1 M  $\text{NH}_4\text{OH}$  buffer solution, and 1-3 M HCl. A cathodic voltammetric peak of  $5.00 \times 10^{-4}$  M As (III) is shown in 4-6 M HCl and its peak current is very small; hardly to observe. It is evident that As (III) in 6 M HCl results a better cathodic voltammogram and gives higher sensitivity for stripping voltammogram (anodic voltammogram). The cathodic voltammogram of As (III) and the anodic voltammogram of arsenic in 6 M HCl are shown in Figure 1. The cathodic peak potential of As (III) is ca. -0.60 V and the anodic

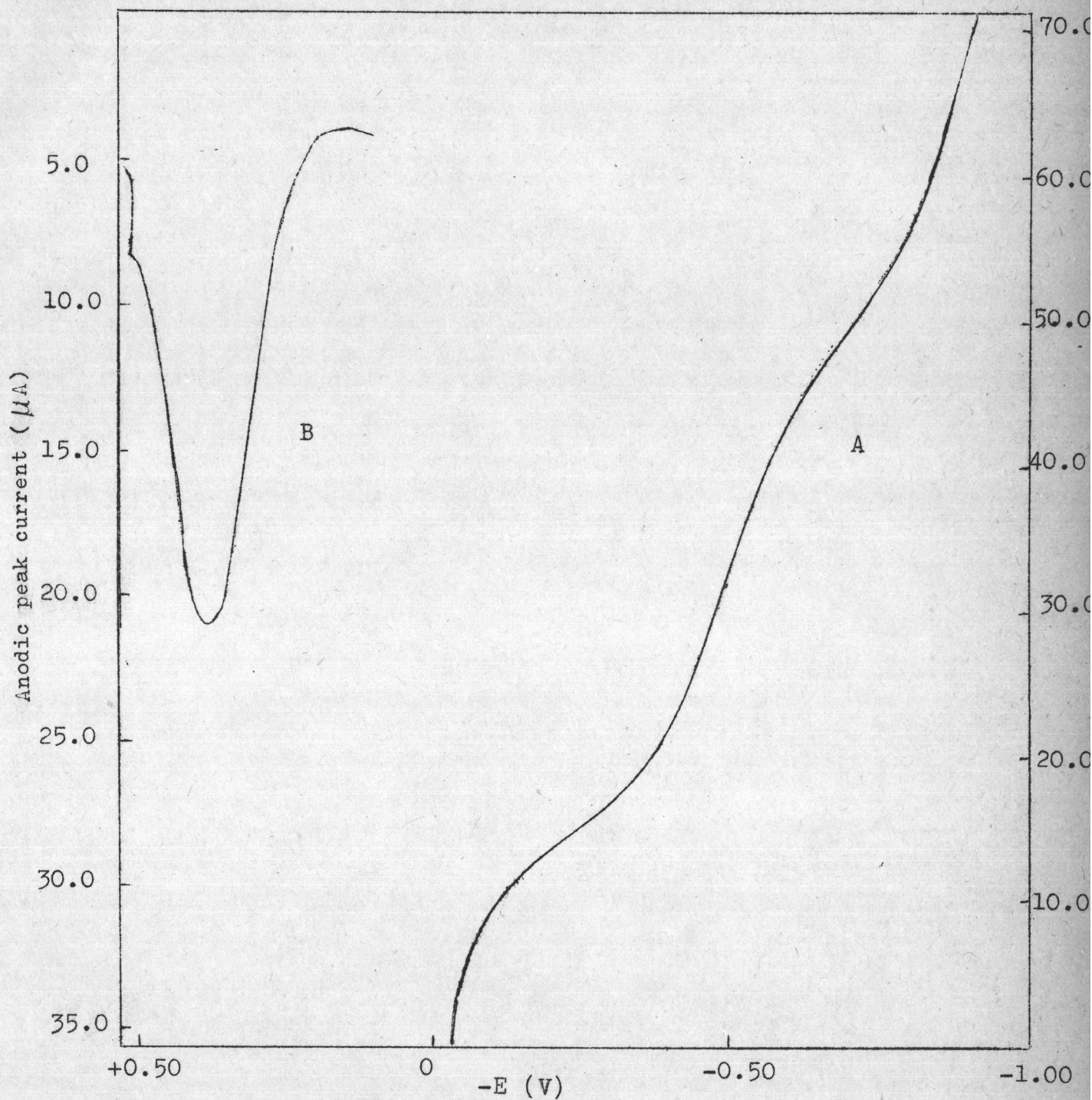


Figure 1 Voltammograms of arsenic in 6. M HCl; A is the cathodic voltammogram of  $5.00 \times 10^{-4}$  M As(III) and B is the anodic voltammogram of arsenic after deposition of  $3.00 \times 10^{-5}$  M As(III) for 3 min.

peak potential of arsenic is ca. +0.40 V. Owing to the limitation of potential scan of the equipment used (-3.00 V to +0.50 V) the anodic voltammogram shows a spike at +0.50 V.

### 3.2 Stripping Analysis

Since the cathodic peak potential of As (III) in 6 M HCl is ca. -0.60 V the deposition potential of -0.60 V is chosen. The time for deposition of As (III) is varied, corresponding to the concentration of As (III) in the test solution. The conditions for deposition of As (III) in 6 M HCl, data of stripping analysis and the detection limit are given in Table 3. The anodic peak current in each condition is directly proportional to the concentration of As (III) as shown in Figure 2. These lines are calculated least squares lines.



Table 3 Conditions for deposition of As (III) and data of stripping analysis of arsenic in 6 M HCl

Deposition		Conc. of As (III) (M)	$i_{p,a}^a$ ( $\mu A$ )	Detection limit (M)
Potential (V)	time (min)			
-0.60	3	$1.00 \times 10^{-4}$	$37.53 \pm 3.48$	$5.00 \times 10^{-6}$
		$5.00 \times 10^{-5}$	$19.17 \pm 1.31$	
		$4.00 \times 10^{-5}$	$16.33 \pm 1.89$	
		$3.00 \times 10^{-5}$	$12.18 \pm 1.18$	
		$2.00 \times 10^{-5}$	$6.78 \pm 0.19$	
		$5.00 \times 10^{-6}$	$1.81 \pm 0.11$	
-0.60	10	$5.00 \times 10^{-6}$	$6.52 \pm 0.49$	$5.00 \times 10^{-7}$
		$4.00 \times 10^{-6}$	$5.02 \pm 0.42$	
		$3.00 \times 10^{-6}$	$4.08 \pm 0.29$	
		$2.00 \times 10^{-6}$	$2.36 \pm 0.25$	
		$1.00 \times 10^{-6}$	$1.38 \pm 0.08$	
		$5.00 \times 10^{-7}$	$0.73 \pm 0.09$	
-0.60	20	$1.00 \times 10^{-6}$	$2.15 \pm 0.23$	$2.00 \times 10^{-7}$
		$5.00 \times 10^{-7}$	$1.02 \pm 0.11$	
		$4.00 \times 10^{-7}$	$0.77 \pm 0.07$	
		$3.00 \times 10^{-7}$	$0.56 \pm 0.04$	
		$2.00 \times 10^{-7}$	$0.35 \pm 0.02$	

<sup>a</sup> average anodic peak current  $\pm$  average deviation of more than 4 trials

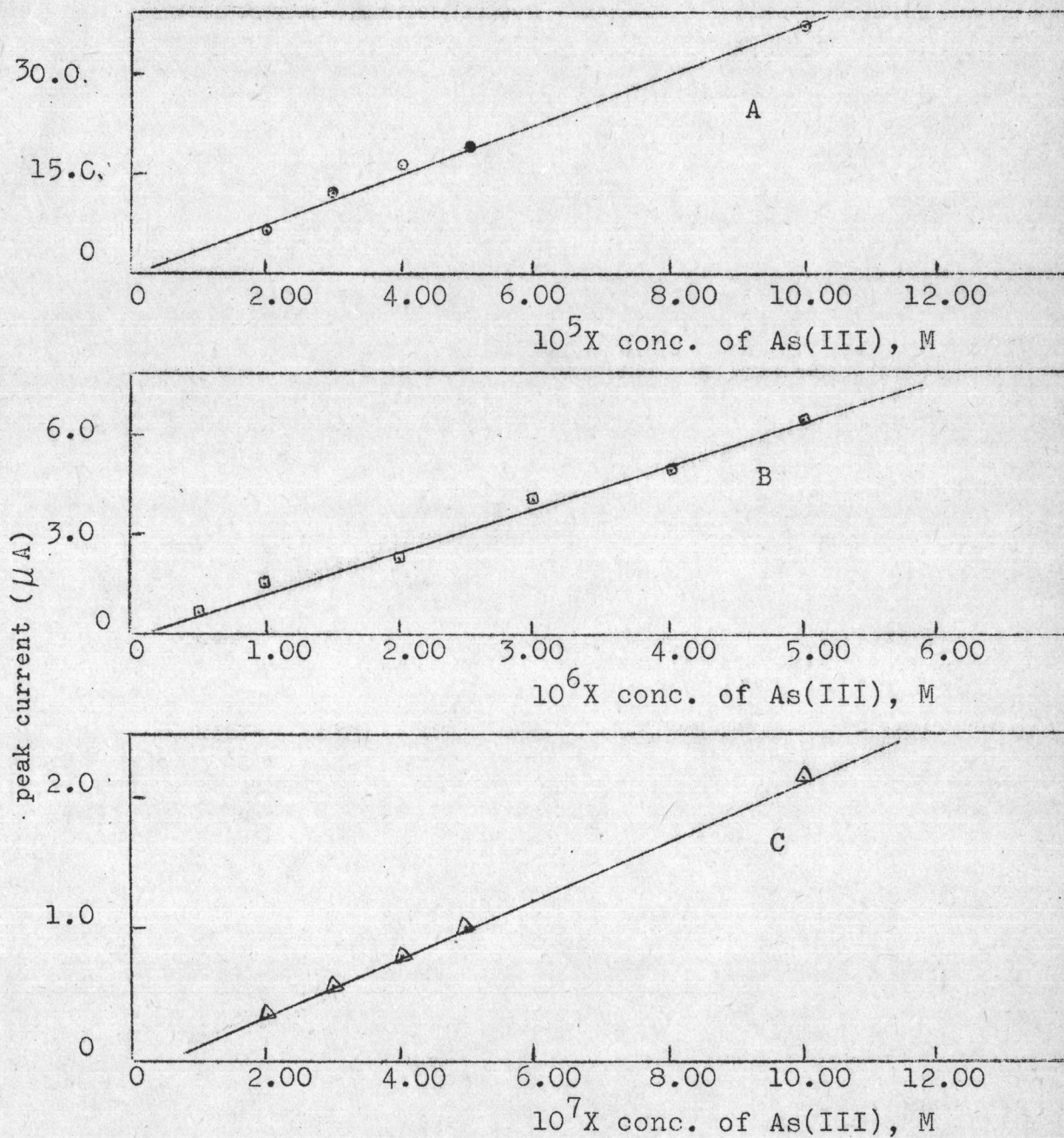


Figure 2 The linear dependence of anodic peak current on concentration for anodic stripping analysis of As(III) using electrodeposition time: A) 3 min, B) 10 min and C) 20 min.