

CHAPTER 5



ANODIC STRIPPING ANALYSIS OF GALLIUM (III)

Polarographic study of gallium in the acetate buffer pH 3.8 resulted in an irreversible process of a 3 electron reduction of gallium pentaacetate anion with a consumption of one proton (109). The polarographic reduction of Ga (III) in aqueous acetylacetone solution was investigated and at pH 3 - 6 the determination of gallium and the simultaneous determination of Ga, In, Pb and Cd were possible (110). The polarographic behavior of Ga (III) was studied in 0.1 M KNO_3 in the presence of the disodium salt of anthranil-N, N-diacetic acid, and the determination of gallium in the range of 5×10^{-5} - 2×10^{-3} M was claimed with the mean error of 2.5% (111). The polarographic determination of gallium from Ag-Ga and Ag-Cu-Ga systems (112) and from gold plating solutions were also described (113). The effects of 25 different organic substances on the half wave potential of Ga (III) reduction in a perchlorate solution on a mercury electrode were studied (114). The mechanism of the polarographic reduction of Ga (III) in the presence of thiocyanate was presented in reference 115. Polarographic behaviors of complexes of Ga (III) with N-cinnamoyl-N-phenylhydroxylamine (29) and with N-phenylcinnamohydroxamic acid (30) were studied in nonaqueous media. In addition, polarographic study of Ga (III) in aqueous melted $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{D}_2\text{O}$, $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was presented in reference 18.

Oscillopolarographic determination of gallium in 0.04 M salicylic acid-0.04 M NaCl at pH 3.7 to 4.5 in the presence of arsenic was proposed (116) as well as gallium in **semi**conductor compounds, GaAs and GaSb, was determined oscillopolarographically in the presence of 6×10^{-3} M gallic acid (117). The oscillopolarographic behavior of gallium was also studied in 0.1 M sodium salicylate at pH 4.45 and in acetate buffer at pH 4.6 (118).

The automatic potentiometric titration of gallium with a standard solution of KOH in isopropyl alcohol was determined in an acetone medium (43), and in dimethylformamide isopropyl alcohol (1:4) solution (119). The amperometric titration of small amount of Ga (III) with 8-mercaptoquinoline in acetate buffer at pH 3.7 - 6.7 was both more accurate and more sensitive than the potentiometric method (120). Biamperometric titration of gallium with EDTA in a medium of acetic acid-benzene was described in reference 92. The amperometric titration of gallium with thiooxime (93) and with uranyl-N, N-diacetic acid (94) were also reported.

An anodic stripping method was developed for the determination of Ga (III) at a rotating Pt electrode by a codeposition with Zn at -1.4 V in 1 M NH_3 and 1 M NH_4Cl (pH 9.6) (121). Inverse voltammetric determinations of gallium in 1 M KCl and 1 M KSCN on a graphite and a mercury-graphite electrode were compared, and Ga (III) was best determined on a mercury-graphite electrode with the optimum pH at 5 - 6 and preelectrolysis potential of -1.5 V vs SCE, as well as gallium in high purity aluminum was determined with a relative standard deviation of

10 - 16% (122). The a.c. phase selective anodic stripping analyses of trace concentrations of gallium in acidified NaSCN-NaClO₄ supporting electrolyte, using the micrometer hanging Hg drop electrode, were reported (123, 124) as well as the millimolar Ga (III) in M NaSCN was determined by a single sweep a.c. phase selective polarography (125). In addition, the a.c. phase selective anodic stripping method for determination of Ga, as mentioned in reference 123, 124 and 125, was applied to analyze Ga in spiked bovine tissues (126).

In this chapter, the cathodic voltammetric behavior of Ga (III) in various supporting electrolytes and the anodic voltammetry of Ga (III) in electrolyte chosen are reported.

5.1 Evaluation of electrolyte

The cathodic voltammetric behavior of 1.00×10^{-3} M Ga (III) in each of the following supporting electrolyte was studied, 0.1 M KNO₃, 1.0 M KCl, 0.1 M HClO₄, 0.1 M - 1.0 M NaSCN, acetate buffer pH 3.6-5.6 and 1 M NH₃- 1 M NH₄Cl buffer (pH 9). No cathodic peak of Ga (III) is produced in 0.1 M HClO₄, acetate buffer pH 3.6 - 5.6 and 1 M NH₃- 1 M NH₄Cl buffer (pH 9). However, a single cathodic peak of Ga (III) is given in 0.1 M KNO₃ at -1.3 V, in 1.0 M KCl at -1.4 V, and in 0.1 M - 1.0 M NaSCN at -1.65 V (see Figure 5.1). Therefore the ASV of Ga (III) was studied in 0.1 M KNO₃, 1 M KCl and 0.1 M - 1.0 M NaSCN. A single anodic peak of gallium is yielded in the ASV of 1.00×10^{-4} M Ga (III) in 0.1 M KNO₃, 1.0 M KCl and 1.0 M NaSCN, using 5 minute

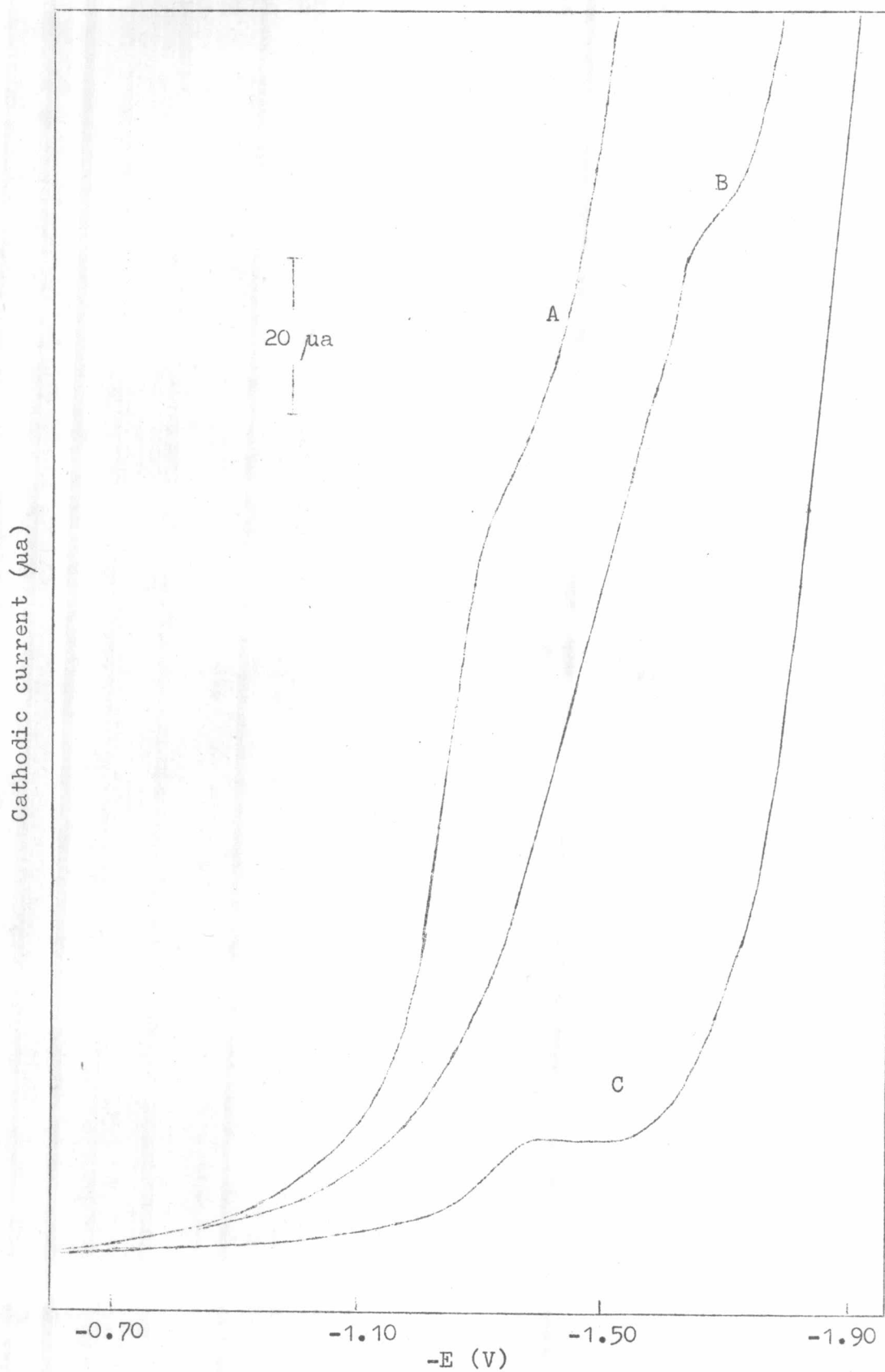


Figure 5.1 Cathodic voltammograms of $1.00 \times 10^{-3} \text{ M Ga (III)}$ in A) 0.1 M KNO_3 , B) 1.0 M NaSCN , and C) 1.0 M KCl .

deposition at -1.5 V, -1.5 V, and -1.7 V, respectively (see Figure 5.2). Two anodic stripping peaks of gallium are also illustrated in 0.1 M NaSCN and 0.5 M NaSCN (see Figure 5.3). The ASV data of 1.00×10^{-4} M Ga (III) in the electrolytes mentioned are compared in Table 5.1. As seen in Table 5.1 the maximum anodic peak current of gallium was obtained in 1.0 M NaSCN, therefore 1.0 M NaSCN was selected as supporting electrolyte for ASV of Ga (III).

5.2 Stripping analysis

Using the deposition of Ga (III) in 1.0 M NaSCN at -1.7 V for 5 minutes, a series of solutions of Ga (III), 8.00×10^{-6} - 1.00×10^{-4} M, was analyzed and the data are shown in Table 5.2. A single anodic peak is obtained in all concentrations of Ga (III) except 8.00×10^{-6} M Ga (III) (see Table 5.2) and the anodic peak current is directly proportional to the concentration of Ga (III) (see Figure 5.4). Another series of concentrations of Ga (III), 1.00×10^{-6} - 1.00×10^{-5} M, was tried by using 10 minute deposition at -1.7 V, and no anodic stripping peak of gallium shows except two small anodic stripping peaks of the supporting electrolyte, 1.0 M NaSCN, show at -0.1 V and -0.5 V (see Figure 5.5). The reason for obtaining two anodic stripping peaks of the supporting electrolyte may be explained by the following mechanism: the 1.0 M NaSCN used is in the acidic medium (pH about 3) as conditioned for Ga (III) stock solution and by a longer deposition time (10 minutes) the supporting electrolyte

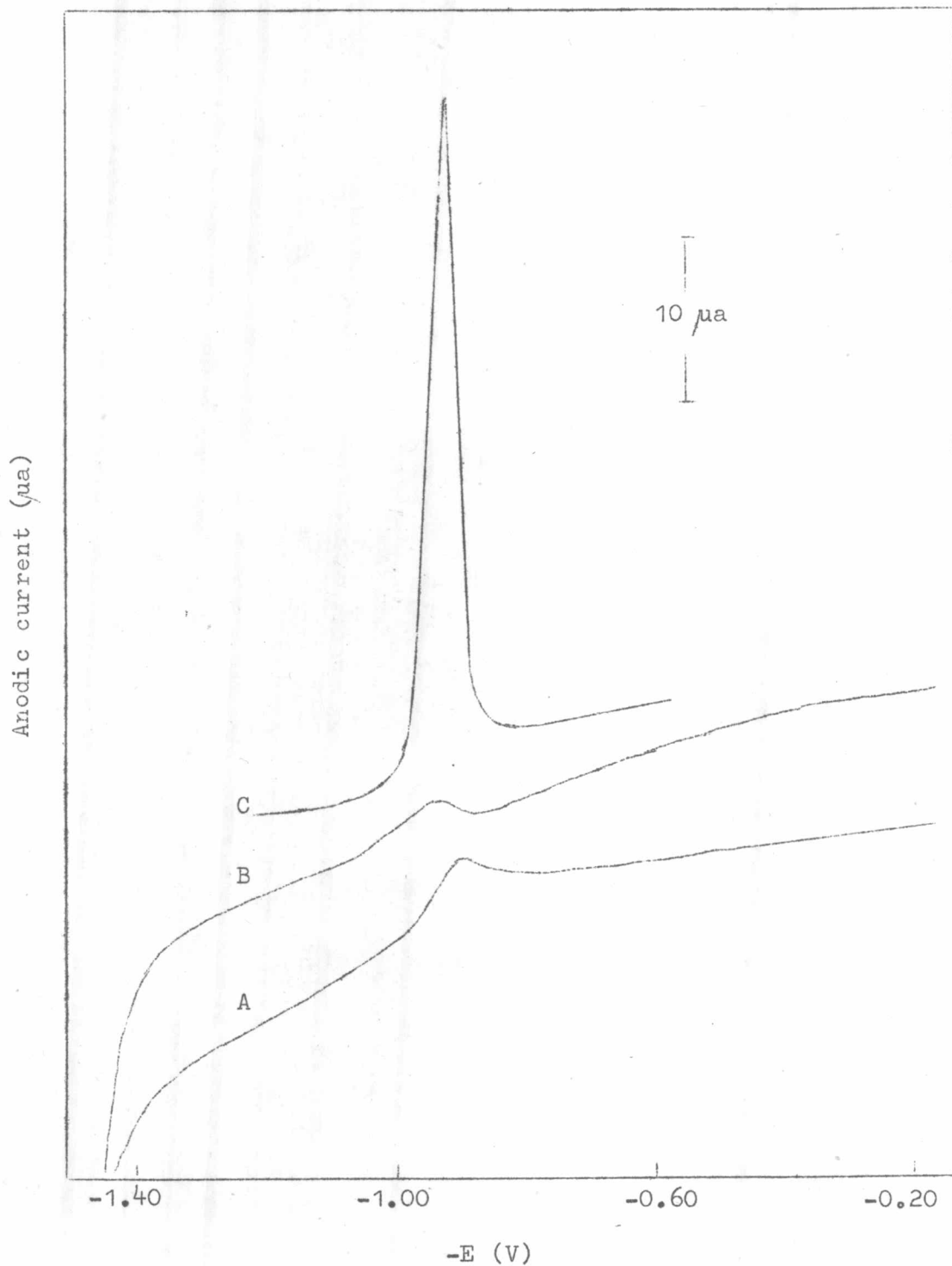


Figure 5.2 Anodic stripping voltammograms of 1.00×10^{-4} M Ga (III) using a 5 minute deposition at -1.5 V in A) 1.0 M KCl, B) 0.1 M KNO₃, and at -1.7 V in C) 1.0 M NaSCN.

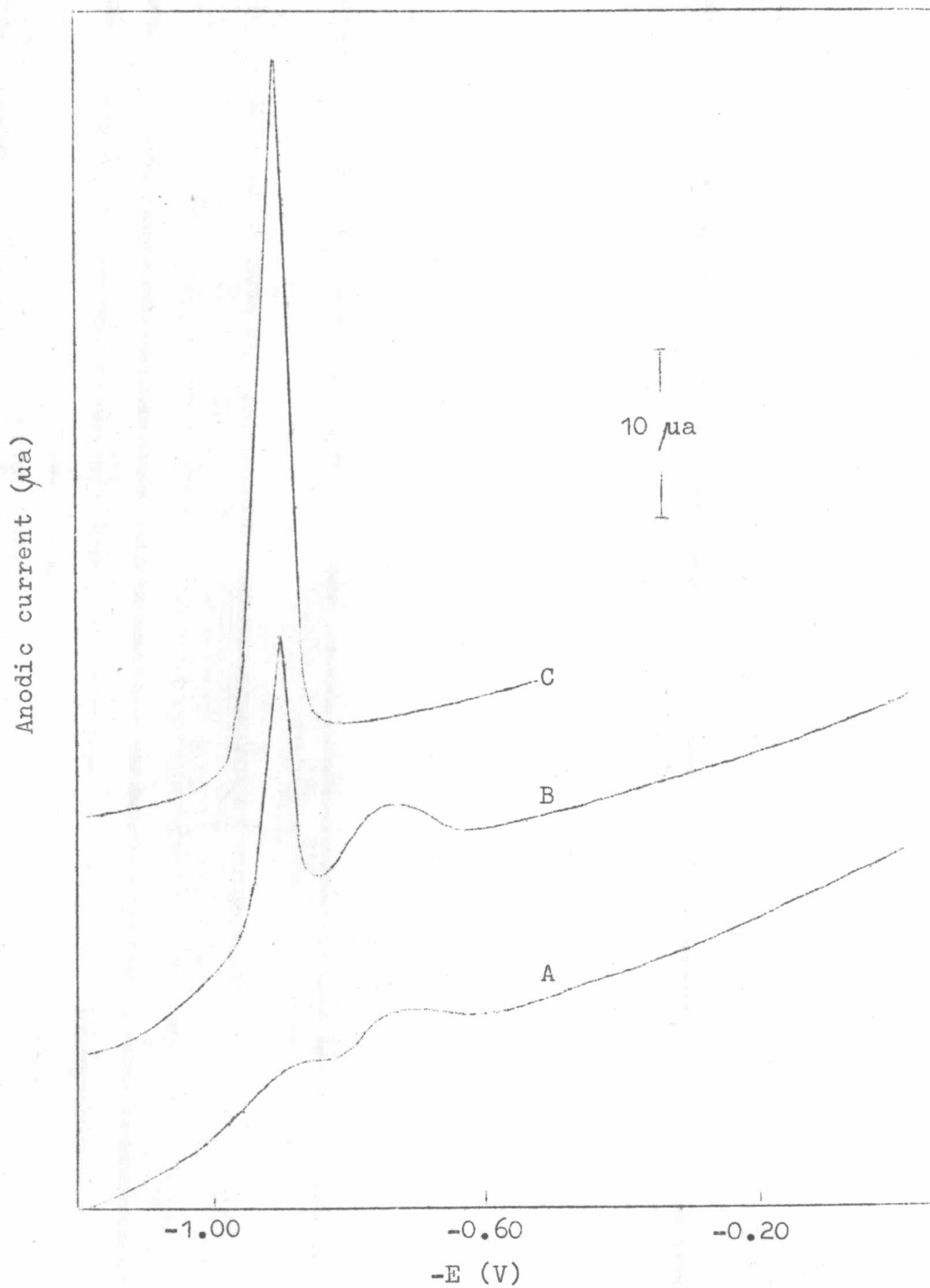


Figure 5.3 Anodic stripping voltammograms of 1.00×10^{-4} M Ga (III) using a 5 minute deposition at -1.7 V in
A) 0.1 M NaSCN, B) 0.5 M NaSCN and
C) 1.0 M NaSCN

Table 5.1 Comparison of ASV data of $1.00 \times 10^{-4} \text{M}$

Ga (III) in the following supporting electrolyte, using a 5 minute electrodeposition.

Supporting electrolyte	deposition potential V	$E_{p, a}$ V	$i_{p, a}$ μa
0.1 M KNO_3	-1.5	-0.92	1.80
1.0 M KCl	-1.5	-0.88	2.10
0.1 M NaSCN	-1.7	-0.89	2.00
		-0.75	2.00
0.5 M NaSCN	-1.7	-0.90	16.00
		-0.75	3.00
1.0 M NaSCN	-1.7	-0.90	42.00
2.0 M NaSCN	-1.7	-0.93	5.00

Table 5.2 The anodic stripping analysis of Ga (III) in 1.0 M NaSCN supporting electrolyte, using a 5 minute deposition at -1.7V

Conc. of Ga (III) M	$E_{p, a}$ V	$i_{p, a}$ μa
1.00×10^{-4}	-0.90	42.0
5.00×10^{-5}	-0.92	26.0
3.00×10^{-5}	-0.92	10.0
1.00×10^{-5}	-0.92	1.75
8.00×10^{-6}	None	None

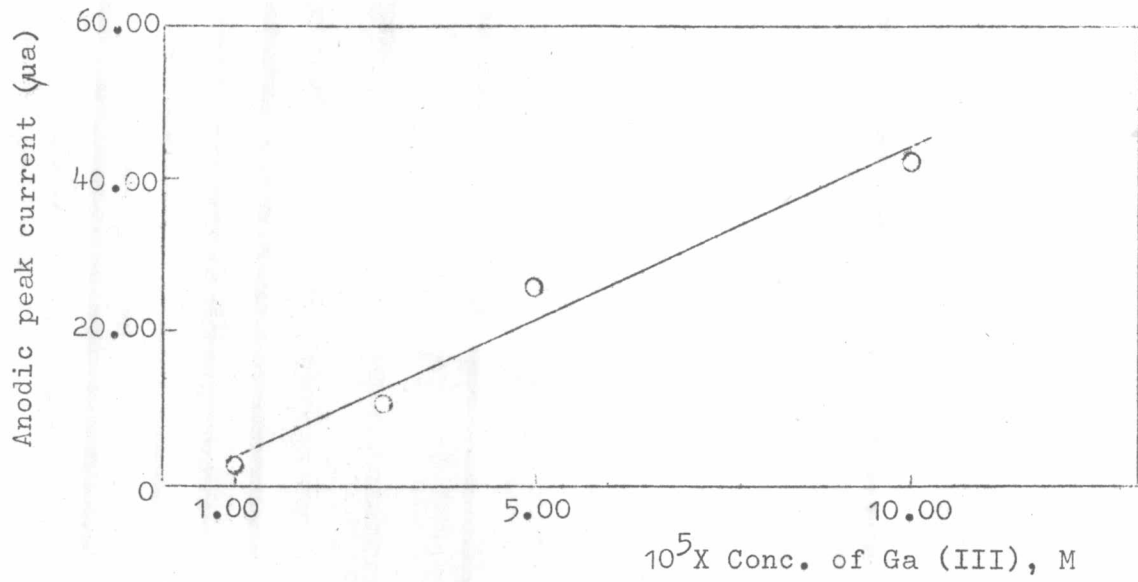


Figure 5.4 Dependence of the anodic stripping peak current of gallium in 1.0 M NaSCN on the concentration of Ga (III)

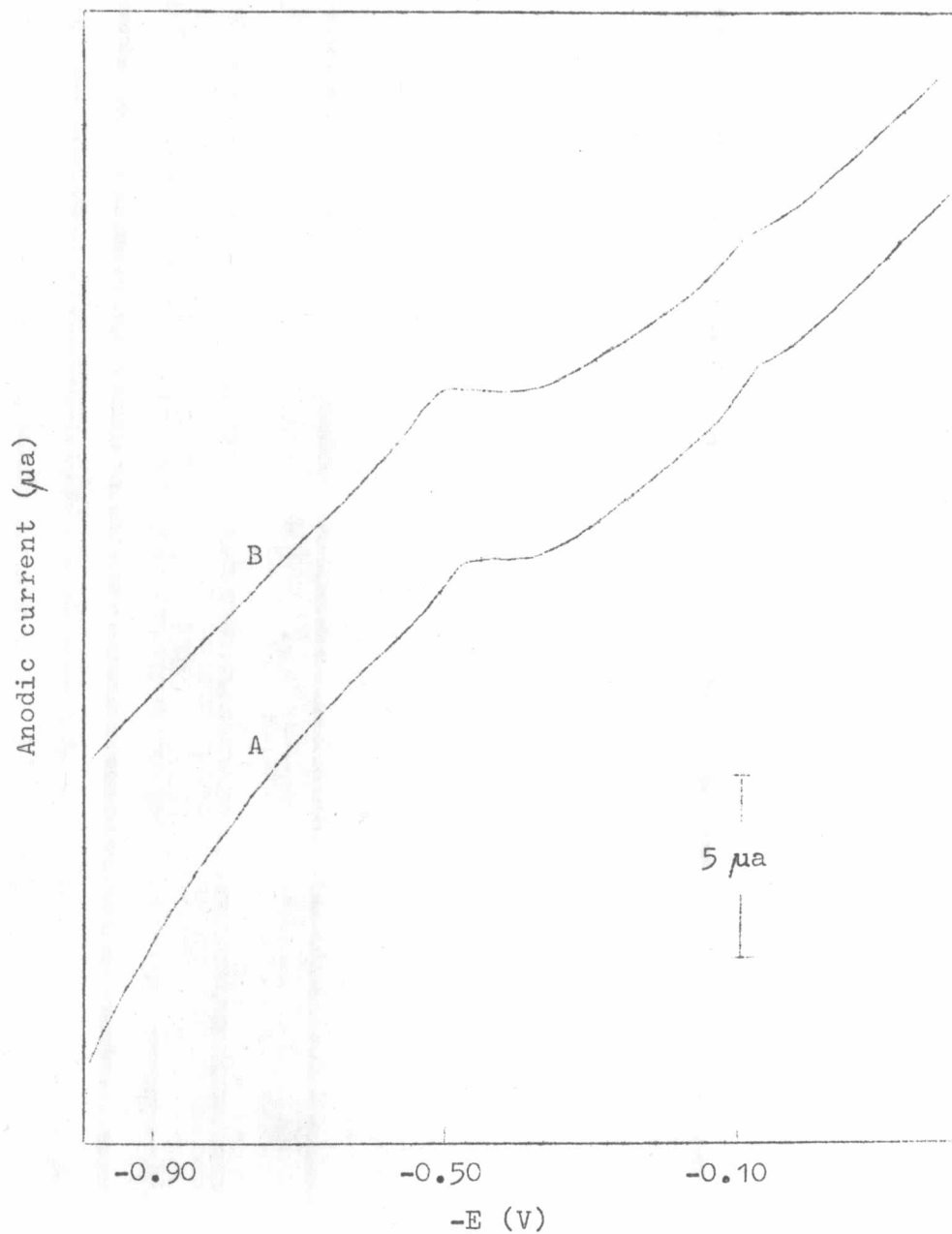


Figure 5.5 Anodic stripping voltammograms of
A) 1.0 M NaSCN (background electrolyte) and
B) 1.00×10^{-5} M Ga (III) in 1.0 M NaSCN
by a 10 minute deposition at -1.7 V.

has been decomposed on the GCE and the decomposed product is then oxidized in the anodic stripping step giving two anodic peaks. Thus, the time used for electrodeposition of metal species in NaSCN supporting electrolyte has to be as short as possible. The detection limit for the determination of gallium by this method is $1.00 \times 10^{-5} \text{ M Ga (III)}$.