CHAPTER 6

ANODIC STRIPPING ANALYSES OF

THALLIUM, INDIUM, AND GALLIUM IN MIXTURES

Polarographic determinations of indium and thallium in indium-
and thallium-doped cesium iodide single crystal were performed in
0.5 M ethylenediamine -0.25 M NH_3- 0.05 M KCl supporting electrolyte
(127). The differential potentiometric titrations of gallium, indium,
and thallium in their binary mixtures were possible with diphenyl-
quanidine in water-acetone solvent(128). The determination of indium
and gallium in semiconductor alloys (In-Ga alloy) by automated
potentiometric titration with 1.0 M KOH in non-aqueous solutions were
also reported (129). In addition, the simultaneous determinations of
components of mixtures of Pb with Tl or In and mixtures of In with
Cd or Tl were proposed by extraction-polarographic method (130).

In this chapter, the anodic stripping analyses of thallium,
indium, and gallium in prepared mixtures are discussed. The limit of
detection of each component in the mixtures is also presented.

6.1 Determination of thallium in the mixture of Tl (I) and In (III)
    and in the mixture of Tl (I) and Ga (III)

    6.1.1 Effect of indium on thallium peak current in 0.1 M KNO_3
          supporting electrolyte

Due to no anodic stripping peak of In (III) obtained in 0.1 M KNO_3 as described in chapter 4, the determination of Tl (I) in the mixture of thallium and indium was firstly studied in 0.1 M KNO_3 supporting electrolyte. A series of In (III) solutions with concentrations of 1.00×10^{-7} M, 5.00×10^{-7} M, 1.00×10^{-6} M, 5.00×10^{-6} M, 1.00×10^{-5} M and 1.00×10^{-4} M In (III) was respectively mixed with 1.00×10^{-4} M Tl (I) solutions. The ASV of these mixtures were then studied by using a 3 minute electrodeposition at -1.0 V, and the data obtained are tabulated in Table 6.1. The single anodic stripping peak obtained is belonged to the anodic stripping analysis of 1.00×10^{-4} M Tl (I) (see chapter 3) and the anodic peak current is plotted against In (III) concentration contained in the mixture (Figure 6.1). It is seen from Figure 6.1 that 1.00×10^{-4} M Tl (I) in the mixture of Tl (I) and In (III) can be determined with no interference from In (III) in the concentration of 1.00×10^{-7} to 1.00×10^{-5} M. However, as the concentration of In (III) in the mixture equals to that of Tl (I), 1.00×10^{-4} M, the anodic stripping peak current of thallium is suppressed (see Table 6.1). The effect of indium on the anodic stripping peak current of thallium was also studied at lower concentrations of Tl (I) in the mixtures, 5.00×10^{-5} M and 5.00×10^{-6} M Tl (I). The results are also listed in Table 6.1. As seen from Table 6.1, 1.00×10^{-6} M to 1.00×10^{-5} M In (III) do not interfere the ASV of 5.00×10^{-5} M Tl (I), as well as 1.00×10^{-7} M to 1.00×10^{-6} M In (III) do not interfere the ASV of 5.00×10^{-6} M Tl (I). It is also observed that In (III) can suppress the anodic stripping peak of Tl (I) as the concentration

Table 6.1 Data of the ASV of mixtures of Tl (I) and In (III) in
0.1 M KNO_3 supporting electrolyte

Composition of the mixture		$E_{p, a}$ V	$i_{p, a}^{*}$ μa
$[Tl^+]$ M	$[In^{3+}]$ M		
A) 3 minute deposition at -1.0 V			
1.00×10^{-4}	1.00×10^{-7}	-0.65	73.00 ± 5.60
1.00×10^{-4}	5.00×10^{-7}	-0.67	73.38 ± 6.45
1.00×10^{-4}	1.00×10^{-6}	-0.67	74.53 ± 10.47
1.00×10^{-4}	5.00×10^{-6}	-0.67	70.41 ± 7.12
1.00×10^{-4}	1.00×10^{-5}	-0.67	74.45 ± 1.05
1.00×10^{-4}	1.00×10^{-4}	-0.75	3.48 ± 0.03
5.00×10^{-5}	1.00×10^{-6}	-0.73	25.90 ± 0.56
5.00×10^{-5}	5.00×10^{-6}	-0.73	24.47 ± 1.01
5.00×10^{-5}	1.00×10^{-5}	-0.74	25.11 ± 0.62
B) 10 minute deposition at -1.0 V			
5.00×10^{-6}	1.00×10^{-7}	-0.79	1.60 ± 0.20
5.00×10^{-6}	1.00×10^{-6}	-0.79	1.60 ± 0.13
5.00×10^{-6}	1.00×10^{-5}	None	None
5.00×10^{-6}	1.00×10^{-4}	None	None

* average anodic peak current $\pm$ average deviation of more than 3 trials.
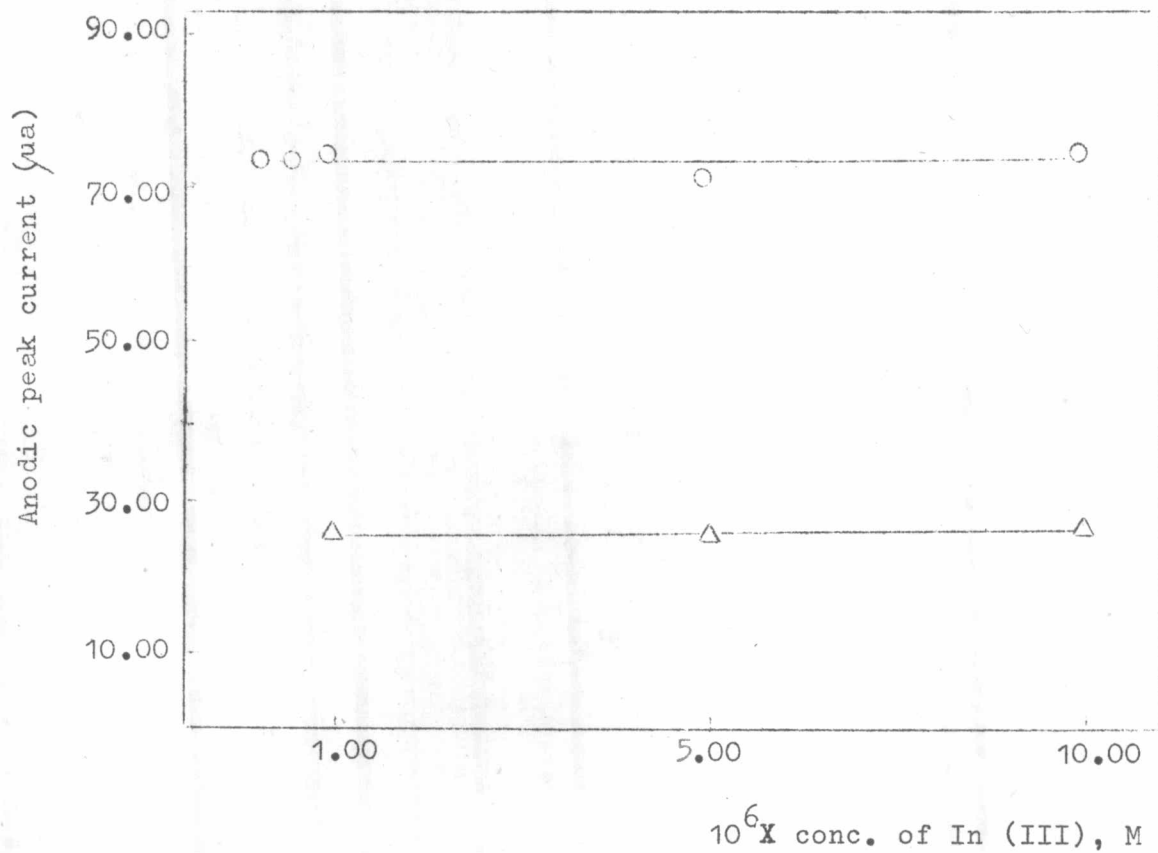
Figure 6.1 Plots of the anodic peak current of Tl (I) vs

the concentration of In (III) in Tl (I)-In (III)

mixture in 0.1 M KNO_3 supporting electrolyte;

△ in the presence of 5.00 X 10^{-5}M Tl (I)

○ in the presence of 1.00 X 10^{-4}M Tl (I).

of In (III) is higher than that of Tl (I) (see Table 6.1 B). Thus, the anodic stripping analysis of Tl (I) in the binary mixture of Tl (I) and In (III) is successful in 0.1 M KNO_3 supporting electrolyte when the concentration of thallium in the mixture is higher than that of indium. Higher concentrations of indium with respect to that of thallium in the mixture (5:1 molar ratio and higher) eliminate anodic stripping peak of thallium (see Table 6.1).

6.1.2 Effect of gallium on thallium peak current in 0.1 M KNO_3 supporting electrolyte

Owing to the anodic peaks of Tl (I) and Ga (III) in 0.1 M KNO_3 appeared at -0.93 V and -1.3 V, respectively, the anodic stripping analysis of Tl (I) in this binary mixture was studied by using the electrodeposition potential of -1.0 V and -1.5 V. Using either electrodeposition potential of -1.0 V or -1.5 V, a single anodic stripping peak is obtained from this binary mixture (see Figure 6.2). This anodic peak at ca. -0.68 V is belonged to that of Tl (I) (see CHAPTER 3). The effect of Ga (III) on the anodic stripping peak of Tl (I) was examined in the binary mixtures of 1.00 X 10^{-4} M Tl (I) and various concentrations of Ga (III). The ASV data obtained are tabulated in Table 6.2. The plot of the anodic stripping peak current vs the concentration of Ga (III) shows no interference from Ga (III) (see Figure 6.3). Thus, the anodic stripping analysis of Tl (I) in the binary mixture of Tl (I) and Ga (III) was possible with no interference from Ga (III).
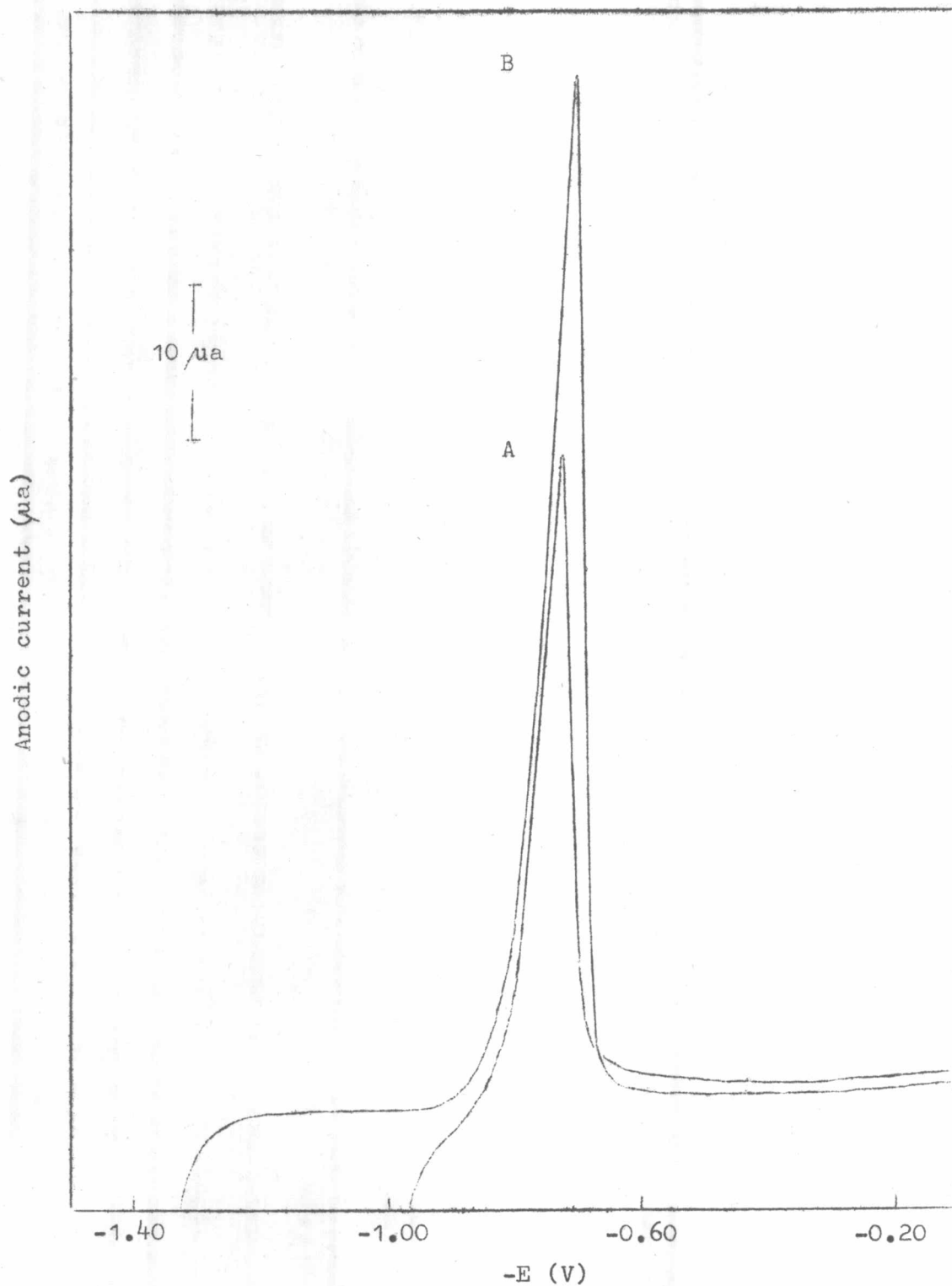
Figure 6.2 The ASV of the binary mixture of 1.00×10^{-5}M Tl (I) and 8.00×10^{-5}M Ga (III) in 0.1 M KNO_3, using a 10 minute electrodeposition at A) -1.0 V and B) -1.5 V.

Table 6.2 Data of the ASV of mixtures of Tl (I) and Ga (III) in

0.1 M KNO_3 supporting electrolyte.

Composition of the mixture		$E_{p,a}$ V	$i_{p,a}^{*}$ /ua
$[Tl^{+}]$ M	$[Ga^{3+}]$ M		
1.00×10^{-4}	1.00×10^{-6}	-0.67	98.3 ± 6.3
1.00×10^{-4}	1.00×10^{-5}	-0.67	101.7 ± 2.7
1.00×10^{-4}	1.00×10^{-4}	-0.67	102.2 ± 1.8
1.00×10^{-4}	1.00×10^{-3}	-0.68	102.5 ± 2.5

* average anodic peak current $\pm$ average deviation of more than

3 trials.

6.2 Determination of thallium and indium in the mixture of Tl (I) and In (III) in the acetate buffer pH 5.0

Since both Tl (I) and In (III) are able to be determined individually by anodic stripping analysis in the acetate buffer pH 5.0 (see CHAPTERS 3 and 4), the anodic stripping analysis of Tl (I) and In (III) in the binary mixture of Tl (I) and In (III) were investigated in the acetate buffer pH 5.0.

A series of binary mixtures of 1.00×10^{-5} M Tl (I) and various concentrations of In (III), 1.00×10^{-5} M, 2.00×10^{-5} M, 5.00×10^{-5}, 8.00×10^{-5} and 1.00×10^{-4} M In (III), was prepared, and the ASV of these mixtures were performed by using 3 minute deposition at -1.0 V.
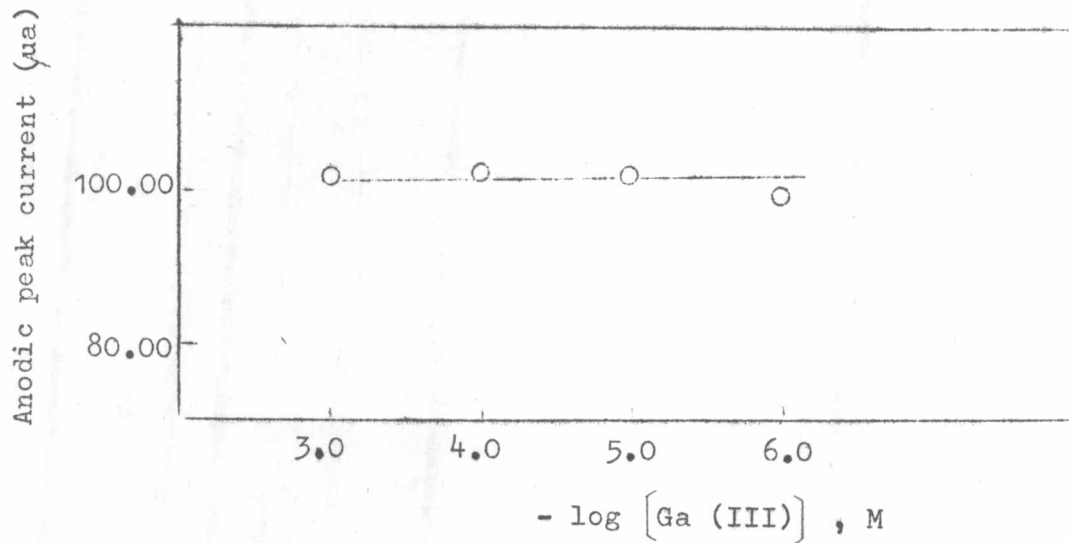
Figure 6.3 The plot of the anodic stripping peak current of Tl (I) vs the log concentration of Ga (III).

The data obtained are shown in Table 6.3. At the molar ratios of Tl (I) to In (III) of 1:1 and 1:2, the stripping voltammogram of each mixture produces two anodic peaks at -0.80 V and ca. -0.71 V (see Figure 6.4) which are the anodic peak of Tl (I) and In (III), respectively (see CHAPTERS 3 and 4). When the molar ratio of Tl (I) to In (III) is less than 1:2 the anodic stripping peak of Tl (I) is smaller and this peak becomes undetectable at the molar ratio of 1:10 (see Table 6.3 and Figure 6.4). On the other hand, the anodic stripping peak current of In (III) increases directly with the concentration of In (III) in the binary mixture (see Figure 6.5).

The other two series of binary mixtures of 1.00×10^{-5}M In (III) and various concentrations of Tl (I), 1.00×10^{-5}M - 1.00×10^{-4}M Tl (I) and 1.00×10^{-6}- 1.00×10^{-5}M Tl (I), were studied by anodic stripping analysis using 3 minute deposition at -1.0 V and 10 minute deposition at -1.0 V, respectively. The data are listed in Table 6.4.

By 3 minute deposition, the anodic stripping voltammograms of the binary mixtures at the molar ratio of 1:1 (Tl (I) to In (III)) shows two anodic peaks at -0.80 V and -0.72 V which refer to that of Tl (I) and In (III), respectively, and at the molar ratio of 2:1 a double peak at -0.74 V and -0.72 V appears (see Figure 6.6). When the molar ratio of Tl (I) to In (III) is 5:1 and higher, one anodic stripping peak is obtained at ca. -0.65 V, this peak may be the super-imposed peak of thallium and indium. However, the anodic stripping peak current obtained is directly proportional to the concentration of Tl (I) in the binary mixture (see Figure 6.7).

Table 6.3 The ASV data of mixtures of 1.00×10^{-5} M Tl (I) and various concentrations of In (III) in the acetate buffer pH 5.0, using 3 minute deposition at -1.0 V.

Composition of the mixture			ASV of Tl (I)		ASV of In (III)	
$[Tl^+]$ M	$[In^+]$ M	molar ratio of Tl(I) to In(III)	$E_{p,a}$ V	$i_{p,a}^*$ μa	$E_{p,a}$ V	$i_{p,a}^*$ μa
1.00×10^{-5}	1.00×10^{-5}	1 : 1	-0.80	1.23 ± 0.02	-0.72	10.32 ± 1.37
1.00×10^{-5}	2.00×10^{-5}	1 : 2	-0.80	1.20 ± 0.05	-0.71	16.50 ± 1.00
1.00×10^{-5}	5.00×10^{-5}	1 : 5	-0.80	cannot be measured	-0.70	32.25 ± 3.13
1.00×10^{-5}	8.00×10^{-5}	1 : 8	-0.80	cannot be measured	-0.70	51.17 ± 3.44
1.00×10^{-5}	1.00×10^{-4}	1 : 10	None	None	-0.66	65.13 ± 2.76

*average anodic peak current $\pm$ average deviation of more than 3 trials.
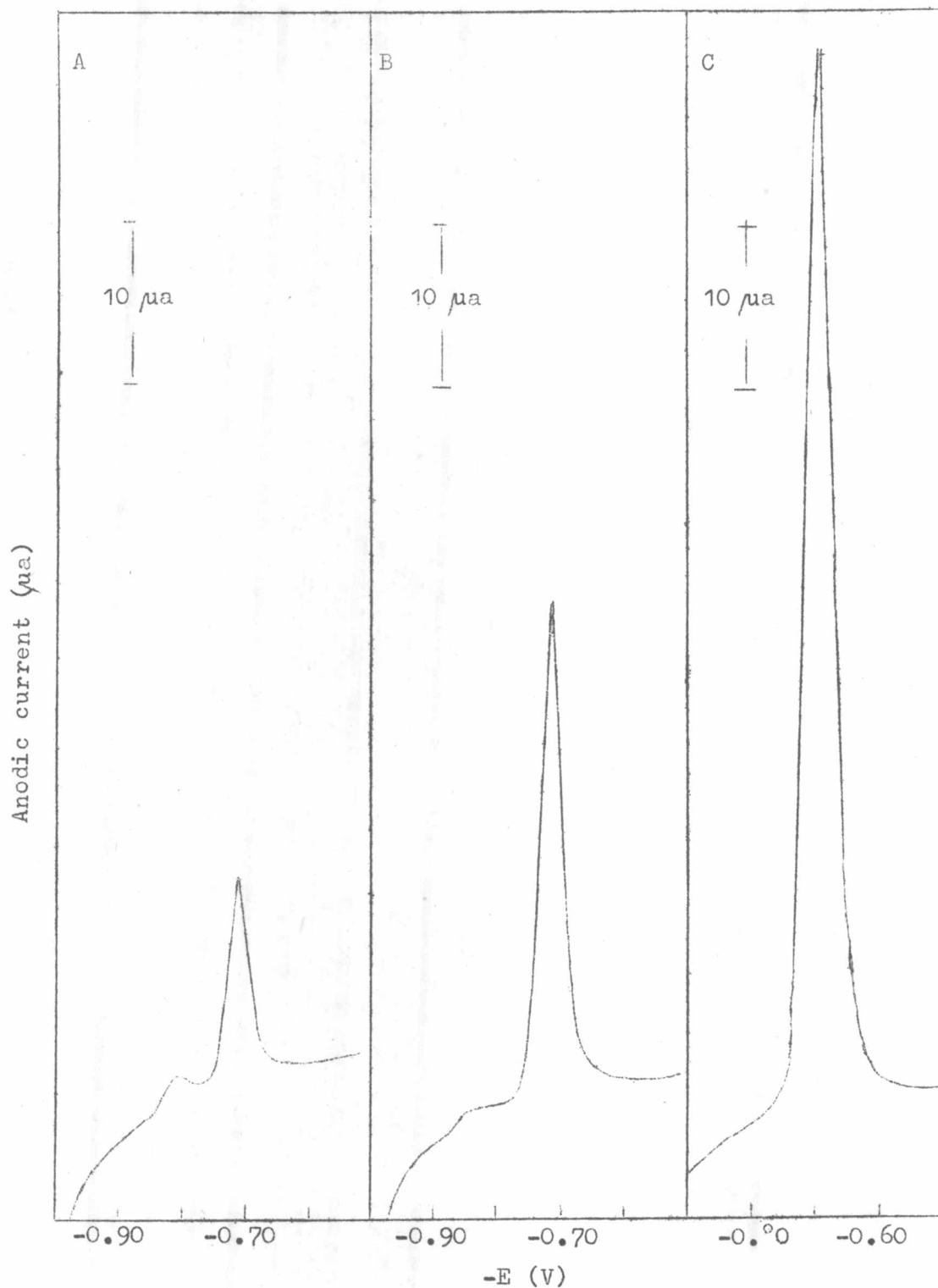
Figure 6.4   The ASV behaviors of Tl (I) - In (III)

mixtures in the acetate buffer pH 5.0 with the molar

ratio of Tl to In of A) 1 : 1, B) 1 : 5 and C) 1 : 10,

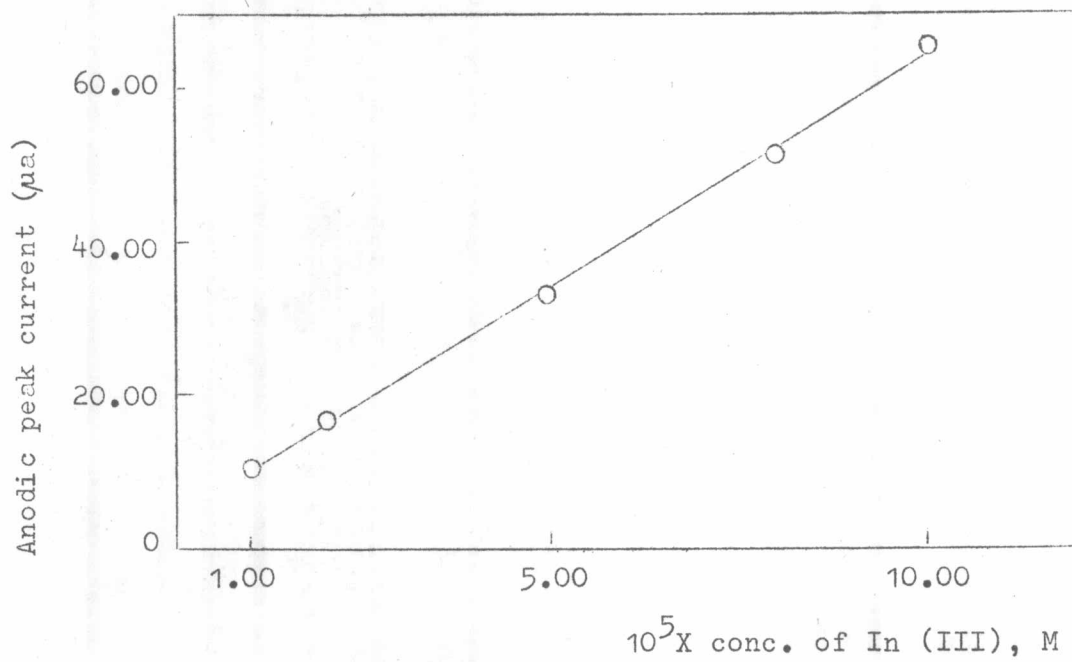using a 3 minute electrodeposition at -1.0 V.

Figure 6.5 The linear dependence of the anodic peak

current at -0.67 V on the concentration

of In (III) in the presence of 1.00 X 10^{-5}M

Tl (I) in acetate buffer at pH 5.0, using

a 3 minute deposition at -1.0 V.

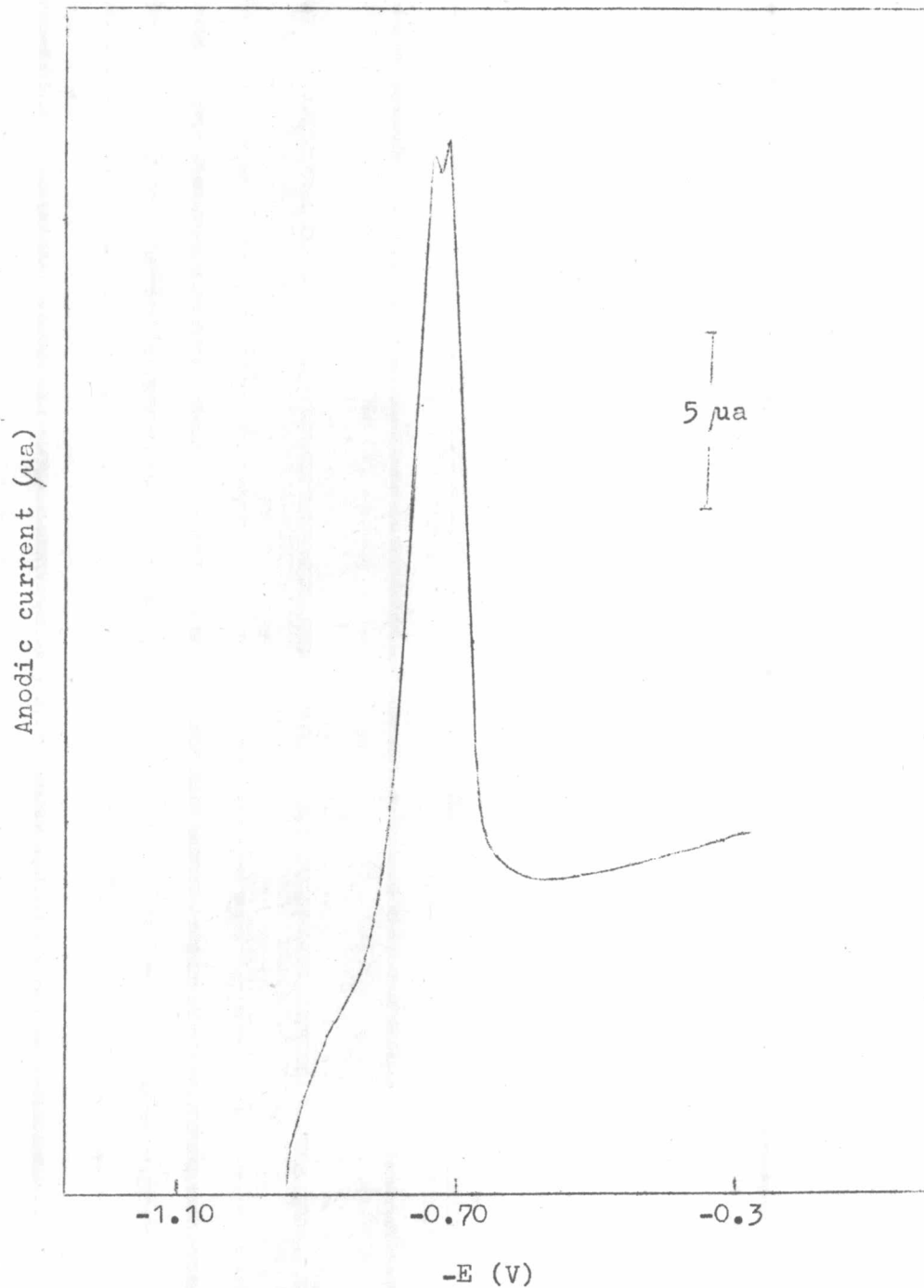Figure 6.6 Anodic voltammogram of the binary mixture
of Tl (I) and In (III) at the molar ratio
of 2:1 (2.00 X 10^{-5}: 1.00 X 10^{-5}) in the
acetate buffer pH 5.0, using a 3 minute
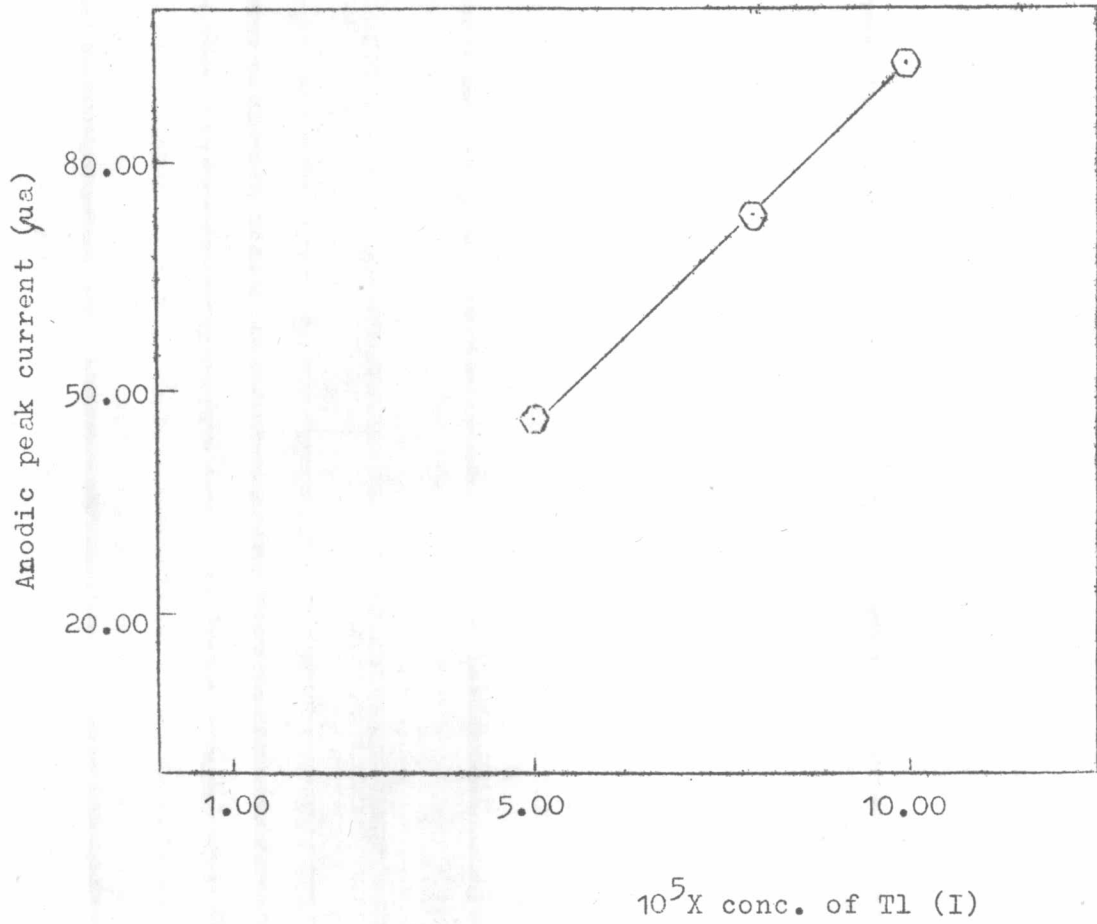deposition at -1.0 V.

Figure 6.7 The plot of the anodic stripping peak current

at ca. -0.65 V vs the concentration of Tl (I)

By 10 minute deposition, the anodic stripping voltammograms
of the binary mixtures at the molar ratio of 1:1 (Tl (I) to In (III))
yields an anodic stripping peak of Tl (I)-In (III) at potential of
-0.70 V and at the molar ratio of 1:2 two anodic stripping peaks appear
at -0.80 V and -0.73 V (see Table 6.4 and Figure 6.8). As the molar
ratio of Tl (I) to In (III) is less than 1:2, an anodic peak of In (III)
appears at -0.73 V and no anodic peak of Tl (I) is obtained (see
Figure 6.8). The plot of the anodic stripping peak current of In (III)
vs the concentration of Tl (I) at the molar ratio of Tl (I) to In (III)
is 1:2 and less shows no interference from Tl (I) (see Figure 6.9).

By this study it is seen that the anodic stripping peaks of
Tl (I) and In (III) are very closed together in the acetate buffer pH 5.0,
and the simultaneous determination of Tl (I) and In (III) is not
possible. However, the anodic stripping analysis of Tl (I) or In (III)
in the binary mixture of Tl (I) and In (III) is successful in the acetate
buffer pH 5 when the concentration of the species desired is at least
twice of the concentration of the other species.

6.3 Determination of Tl (I), In (III) and Ga (III) in the tertiary
mixture of Tl (I), In (III) and Ga (III)

6.3.1 in 0.1 M KNO_3 supporting electrolyte

To study the effect of In (III) and Ga (III) on Tl (I),
a series of tertiary mixtures of 1.00×10^{-4} M Tl (I), 1.00×10^{-6} M
In (III) and various concentrations of Ga (III), $1.00 \times 10^{-6} - 1.00 \times 10^{-3}$ M

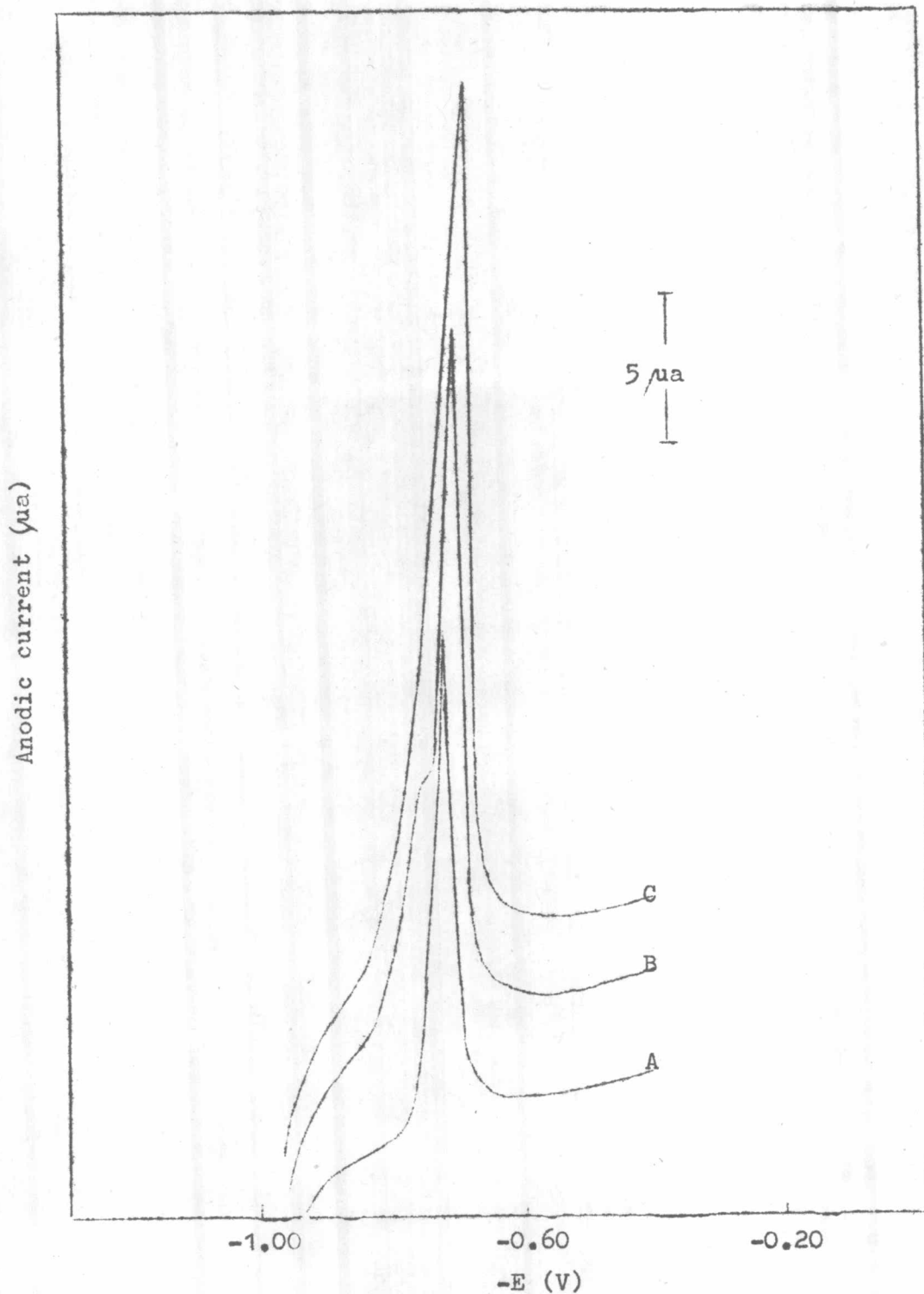Figure 6.8 Anodic stripping voltammograms of binary mixtures
of 1.00 X 10^{-5}M Tl (I) and various concentrations
of In (III) for the molar ratios of A) 1:5,
B) 1:2 and C) 1:1, using a 10 minute deposition
at -1.0 V.

Table 6.4 The ASV data of mixtures of 1.00×10^{-5} M In (III) and various concentrations of Tl (I) in the acetate buffer pH 5.0.

Composition of the mixture			ASV of Tl (I)		ASV of In (III)	
$[Tl^+]$ M	$[In^{3+}]$ M	molar ratio of Tl(I) to In(III)	$E_{p,a}$ V	$i_{p,a}^*$ μa	$E_{p,a}$ V	$i_{p,a}^*$ μa
A) 3 minute deposition at -1.0 V						
1.00×10^{-5}	1.00×10^{-5}	1 : 1	-0.80	1.23 ± 0.02	-0.72	10.32 ± 1.37
2.00×10^{-5}	1.00×10^{-5}	2 : 1	-0.74		-0.72	
5.00×10^{-5}	1.00×10^{-5}	5 : 1	$45.80 \pm 3.47 \mu a$ at -0.68 V			
8.00×10^{-5}	1.00×10^{-5}	8 : 1	$72.77 \pm 2.84 \mu a$ at -0.66 V			
1.00×10^{-4}	1.00×10^{-5}	10 : 1	$92.75 \pm 1.80 \mu a$ at -0.65 V			
B) 10 minute deposition at -1.0 V						
1.00×10^{-6}	1.00×10^{-5}	1 : 10	None	None	-0.71	17.75 ± 0.25
2.00×10^{-6}	1.00×10^{-5}	1 : 5	None	None	-0.72	17.63 ± 1.38
3.00×10^{-6}	1.00×10^{-5}	3 : 10	None	None	-0.73	18.12 ± 0.13
5.00×10^{-6}	1.00×10^{-5}	1 : 2	-0.80	cannot be measured	-0.73	17.25 ± 0.25
1.00×10^{-5}	1.00×10^{-5}	1 : 1	$26.64 \pm 1.96 \mu a$ at -0.70 V			

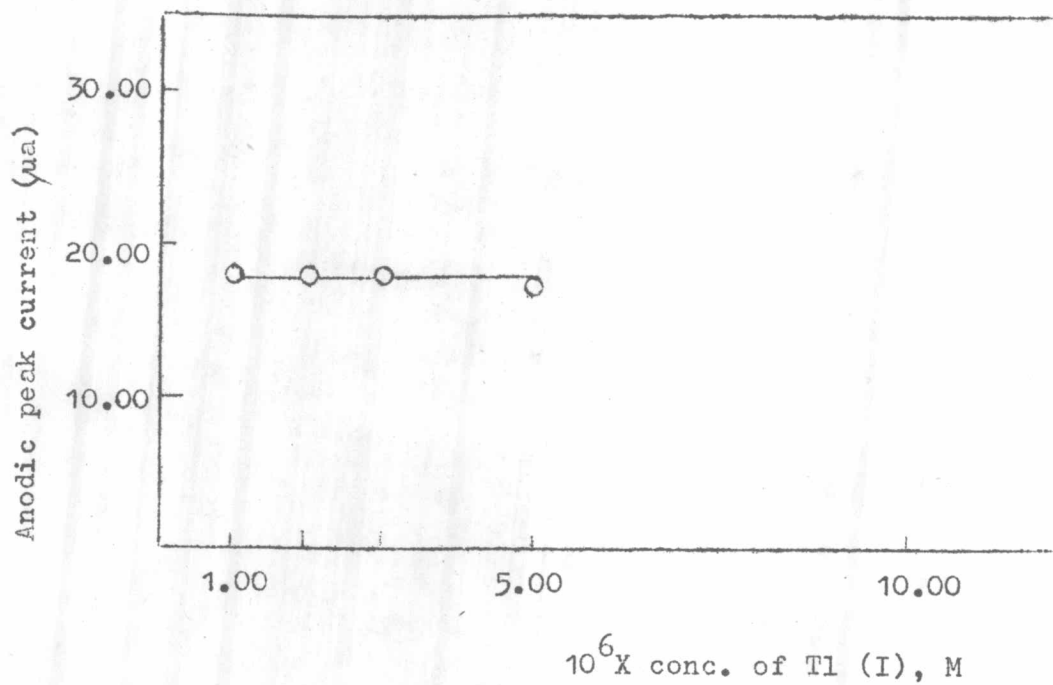* average anodic peak current $\pm$ average deviation of more than 3 trials.

Figure 6.9 The plot of the anodic stripping peak
current of In (III) vs the concentration
of Tl (I).

as well as another series of tertiary mixtures of 1.00×10^{-4} M Tl (I), 2.00×10^{-6} M In (III) and 1.00×10^{-6} M – 1.00×10^{-3} M Ga (III) were investigated by the anodic stripping method in 0.1 M KNO_3.

The ASV data are tabulated in Table 6.5 and the anodic stripping voltammogram is shown in Figure 6.10. Only one anodic stripping peak of Tl (I) is produced from each of the tertiary mixture studied. The plot of the anodic stripping peak current obtained vs the concentration of Ga (III) in the mixture shows no interference from Ga (III) (see Figure 6.11).

6.3.2 in the acetate buffer pH 5.0

Corresponding to no cathodic peak of Ga (III) produced in the acetate buffer pH 5.0, and also no anodic stripping peak appeared even electrodeposition for 10 minutes at -1.0 V, the effect of Ga (III) to Tl (I) and In (III) was not attempted to study in the acetate buffer pH 5.0

6.3.3 in 1.0 M NaSCN

The anodic stripping analysis of components in Tl-In-Ga mixture was not studied in NaSCN supporting electrolyte because all three species can form complexes with thiocyanate ion and the anodic stripping voltammogram of the mixture would result in a complicated one.

Table 6.5   The ASV data of Tl (I)-In (III)-Ga (III) mixtures in
0.1 M KNO_3 supporting electrolyte, using a 3 minute
deposition at −1.0 V.

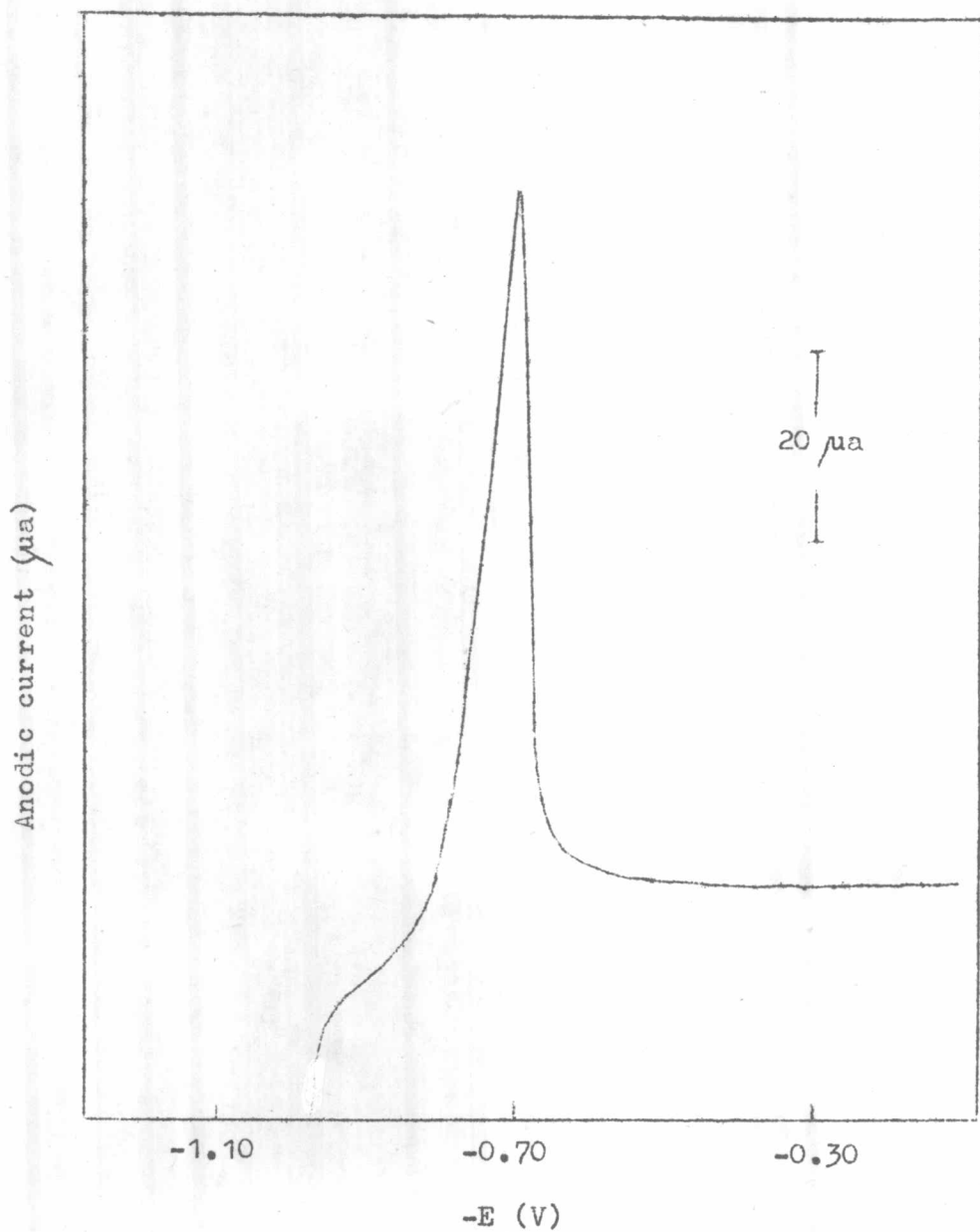| Composition of the mixture			$E_{p, a}$ V	$i_{p, a}$ μa
$[Tl^+]$ M	$[In^{3+}]$ M	$[Ga^{3+}]$ M		
1.00×10^{-4}	1.00×10^{-6}	1.00×10^{-6}	−0.68	74.53
1.00×10^{-4}	1.00×10^{-6}	2.00×10^{-6}	−0.68	78.68
1.00×10^{-4}	1.00×10^{-6}	1.00×10^{-5}	−0.68	74.53
1.00×10^{-4}	1.00×10^{-6}	1.00×10^{-4}	−0.68	73.97
1.00×10^{-4}	1.00×10^{-6}	1.00×10^{-3}	−0.69	74.53
1.00×10^{-4}	2.00×10^{-6}	1.00×10^{-6}	−0.69	76.50
1.00×10^{-4}	2.00×10^{-6}	2.00×10^{-6}	−0.69	74.50
1.00×10^{-4}	2.00×10^{-6}	1.00×10^{-5}	−0.69	74.50
1.00×10^{-4}	2.00×10^{-6}	1.00×10^{-3}	−0.70	74.00

Figure 6.10 Anodic voltammogram of the tertiary mixture of Tl-In-Ga at the concentration of 1.00×10^{-4}, 2.00×10^{-6} and 1.00×10^{-5} M, respectively, in 0.1 M KNO_3 ; using a 3 minute deposition at -1.0 V.
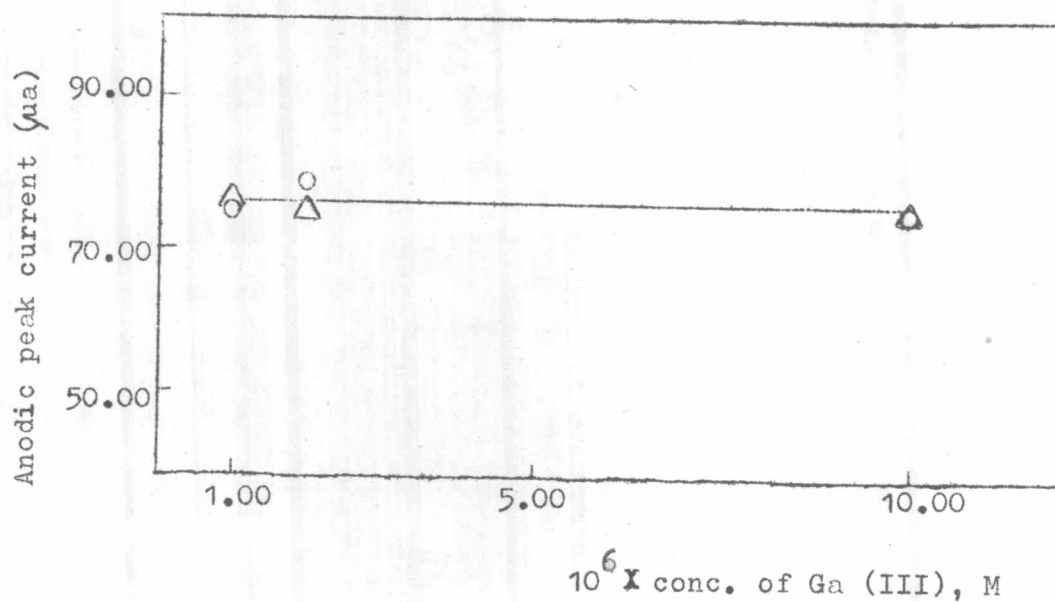
Figure 6.11 The effect of Ga (III) and In (III) on

the anodic stripping peak current of Tl (I)

in 1.00 X 10^{-4}M Tl (I), 1.00 X 10^{-6}M In (III)

and various concentrations of Ga (III) (O)

and in the mixture of 1.00 X 10^{-4}M Tl (I),

2.00 X 10^{-6}M In (III) and various concentra-

tions of Ga (III) (△).