

## Electrochemical Study of Thallium(I) in Thiamine Hydrochloride and Pyruvate and Simultaneous Determination of it with Some Metal Ions

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The polarographic behavior of thallium(I) has been studied using thiamine hydrochloride and pyruvate as complexing agents at constant ionic strength ( $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ ). At the dropping mercury electrode, thallium(I)-pyruvate or thiamine chelate ions give a single well-defined reversible wave both d.c. and a.c. polarographically, and the rate of reduction is diffusion controlled. Thallium(I) is found to form 1 : 1 metal to ligand complex with both ligands, and this composition is supported by the conductometric titration. The formation constant values have been calculated. Pyruvate and thiamine were used as the supporting electrolytes for the a.c. polarographic determination of thallium with lead or copper, cadmium and selenium simultaneously.

### INTRODUCTION

Thallium(I) and its salts have long been known<sup>1-5</sup> to be poisonous to human beings, although radio thallium is used in monitoring cardiac functions. Toxic nature of this element necessitates its detection and determination in micro quantities. Also, thiamine is present in all living organisms and is essential to life. Co-carboxylase, which is widely used in medicine, is a diphosphoric acid ester of thiamine. Co-carboxylase appears as a component of the metalloenzymes which catalyze the decarboxylation of  $\alpha$ -ketoacids and some other biochemical reactions. In order to understand and simulate these vital processes, it is very important to study the complexing properties of thiamine. Fridman *et al.*<sup>6-8</sup> and Grinberg *et al.*<sup>9</sup> have studied the complexing properties of thiamine with some divalent metal ions.

The metal complexes of pyruvate are important due to essential biological role of pyruvic acid. Consequently the metal complexes containing pyruvic acid acquire special consideration<sup>10-11</sup>.

The simultaneous determination of metals at trace levels *e.g.*, in biological matrices or environmental samples has aroused much interest in recent years<sup>12-14</sup>.

Neub and co-workers<sup>15-17</sup> added complexing agents to eliminate interferences; also Dhaneswar and Zarakpar<sup>18</sup> determined lead and thallium in silicon as well as in environmental particulate matter and rain water samples by using a tartrate

buffered medium at pH 4.5 in presence of EDTA. Brukenstein and Nagai<sup>19</sup> developed an interesting method for determination of thallium in presence of lead with a mercury film electrode and chemical stripping. 0.1 M acrylamide<sup>20</sup> (pH = 5.8) and 0.2 M piperazine<sup>21</sup> were used as the supporting electrolytes for the polarographic determination of thallium in presence of some metals.

## EXPERIMENTAL

The polarograms were recorded with an AC/DC Sargent-Welch model 3001 polarograph. Three electrodes were used: dropping mercury electrode as the working electrode and a saturated calomel electrode (SCE) and a platinum electrode were employed as the reference and auxiliary electrodes respectively. The working dropping electrode was a capillary which had the following parameters:  $m = 1.85 \text{ mg sec}^{-1}$  and  $t = 3.25 \text{ sec}$  (open circuit). The voltammetric cell was kept at  $25^\circ \pm 0.5^\circ \text{C}$ . Prior to analysis the solutions were deaerated by purging with pure nitrogen for about 20 min. Standard additions were made with micropipette with disposable plastic tips. The pH values of the solutions were measured with a glass electrode pH meter type WGPYE model 290. Conductometric titrations were carried out on a YSI conductance bridge model 31 using an immersion cell.

All the chemicals used were of AnalaR grade and were dissolved in double-distilled water. Sodium nitrate was used as supporting electrolyte with constant ionic strength (0.1 M). Aqueous stock solutions (0.01 M) of Tl(I), Pb(II), Cd(II), Cu(II) and Se(IV) were prepared. Stock solutions of thiamine hydrochloride and pyruvate (B.D.H.) used were prepared by dissolving the appropriate amount in double-distilled water.

## RESULTS AND DISCUSSION

The polarographic behavior of thallium in thiamine hydrochloride or pyruvate was studied at a constant ionic strength  $\mu = 0.1 \text{ M NaNO}_3$ . A thallium(I)-ligand (thiamine or pyruvate) chelate gives a single well-defined d.c. polarogram; its limiting current was found to be proportional to the square root of the effective pressure of mercury applied to the DME. The relation between  $\log(i/i_d - i)$  and  $E$  gave a straight line with a slope of 58 mV, corresponding to a one electron reduction.

In a.c. polarography, also, typical polarograms were obtained, their summit potentials coincided with the half-wave potential of the d.c. polarogram. This may mean that the electrode reaction of a Tl(I)-ligand (thiamine or pyruvate) chelate proceeds reversibly in the a.c. polarographic sense.

To be more exact, the reversibility of the electrode reaction at the electrode, which is polarized under the influence of an a.c. voltage of a small amplitude, should be tested by the a.c. log-plot method, *i.e.*, the plot of  $\log [(I_p/I)^{1/2} - (I_p/I)^{1/2}]$  against  $E$ , where  $I_p$  and  $I$  are the peak height and the height of a.c. polarogram at a given value of  $E$ , respectively.

The well-known relation (2) of the a.c. polarographic current derived for the following electrode reaction<sup>22,23</sup>:



holds only when the reaction proceeds reversibly in the polarographic sense:

$$I = (n^2 F^2 \cdot A / 4RT) \cdot D_0^{1/2} \omega^{1/2} C_0 \Delta E \cdot \operatorname{sech}^2 [(nf/2RT)(E - E_{1/2})] \cdot \sin(\omega t + \pi/4) \quad (2)$$

The notation definitions are as follows:

$n$  = number of electrons involved in the electrode reaction.

$F$  = Faraday's constant

$A$  = electrode area

$D$  = ideal gas constant,

$T$  = absolute temperature

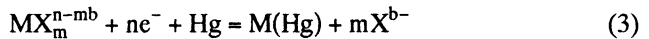
$D_0$  = diffusion coefficient of the species  $D$

$C_0$  = bulk concentration of the species

$\omega$  = Frequency,  $\Delta E$ , amplitude of the applied alternating potential (10mv in the present work)

$E_{1/2}$  = reversible polarographic half-wave potential for the electrode reaction.

Similarly, in the reduction of a metal complex,



When the boundary condition (4), which shows conclusively that the electrode reaction (3) is reversible, is satisfied by the system under the a.c. polarographic conditions, the relation (5) can be obtained by the mathematical treatment employed by Matsuda<sup>22</sup> and Delmastro<sup>23</sup> to derive the relation (2):

$$(C_{MX_m} / C_{M(Hg)})_{x=0} = \theta \cdot \exp[-\gamma \sin \omega t] \quad (4)$$

where  $\theta = \exp [nF/RT(E - (E_{1/2})_c)]$ ,  $\gamma = nf \cdot \Delta E/RT$

$$(E_{1/2})_c = E_{M(Hg)}^0 + RT/nF [\ln K_{M(Hg)} \cdot f_c/K_c - \ln K_c - m \cdot \ln C_x \cdot f_x]$$

where  $E$  = d.c. potential applied

$E_{M(Hg)}^0$  = standard potential

$K_s$  = diffusion current constants

$f$  = activity constants

$C_x$  = the concentration of  $X^{b-}$  at the electrode surface

$K_c = MX_m^{n-mb} / [M^{n+}] \cdot [X^{b-}]^m$ .

$$I = \left( \frac{n^2 F^2 A}{4RT} \right) \cdot D_{MX_m}^{1/2} \cdot \omega^{1/2} \cdot C_{MX_m} \cdot \Delta E X \operatorname{sech}^2 \left[ \left( \frac{nF}{2RT} \right) (E - (E_{1/2})_c) \right] \cdot \sin(\omega t + \pi/4) \quad (5)$$

By casting the relation (5) into logarithmic form and by rearranging the resulting equation, one can obtain the following equation at 25°C:

$$E = (E_{1/2})_c + 2X \cdot 0.591/n \log [(I_p/I)^{1/2} - ((I_p - I)/I)^{1/2}] \quad (6)$$

Here  $I_p$  represents the peak height of the a.c. polarogram of  $MX_m^{n-mb}$ .

The relation (6), clearly indicates that the summit potential in a.c. polarography

can be safely equated with the half-wave potential in d.c. polarography when the electrode reaction is reversible, even under a.c. polarographic conditions; that the plot of  $E$  against  $\log [(I_p/I)^{1/2} - ((I_p - I)/I)^{1/2}]$  gives a straight line with a slope of  $\pm 0.18/nV$  and that the potential can be determined as the potential where  $\log [(I_p/I)^{1/2} - ((I_p - I)/I)^{1/2}]$  is zero.

A typical example of an a.c. log plot is shown in Fig. 1. The slopes found were +96 mV and -106 mV respectively.

The complex formation between thiamine hydrochloride or pyruvate and  $Tl(I)$  ion has been investigated in presence of 0.1 M  $NaNO_3$  as supporting electrolyte ( $\mu = 0.1$ ). A linear relation between  $\Delta E_p$  and  $\log [\text{ligand}]$  is found as shown in Fig. 2. The basic relationship between potential shift and the ligand concentration

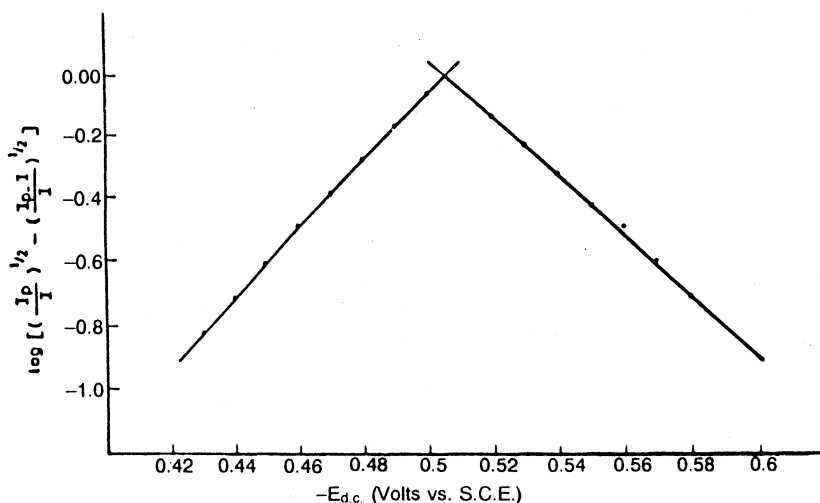


Fig. 1 A test for reversibility of the a.c. electrode process  $Tl(I) + e \rightleftharpoons Tl$  (amalgam) in 0.1 M  $NaNO_3$  and 0.1 M thiamine.

can be expressed by Lingan's equation<sup>24</sup>

$$E_p^c - E_p^s = \frac{0.0591}{n} \log K_f - \frac{0.059}{n} p \log [X]$$

where  $E_p^c$  is the peak potential of the complexed ion in the presence of ligand with concentration  $X$ ,  $E_p^s$  is the peak potential in the absence of ligand (aquo metal ion),  $n$  is the number of electrons gained in the reduction,  $K_f$  is the apparent formation constant and  $p$  is the complex coordination number. It is found that the slopes of the straight lines obtained (Fig. 2) are 0.03 and 0.049 for pyruvate-thallium and thiamine-thallium systems respectively. Accordingly, the coordination number is approximated to one and the stoichiometry of apparent complex formed between  $Tl(I)$  and pyruvate or thiamine is 1:1 ratio. The logarithmic values of stability constants are 3.7 and 2.08 for pyruvate- $Tl(I)$  and thiamine- $Tl(I)$  complexes respectively.

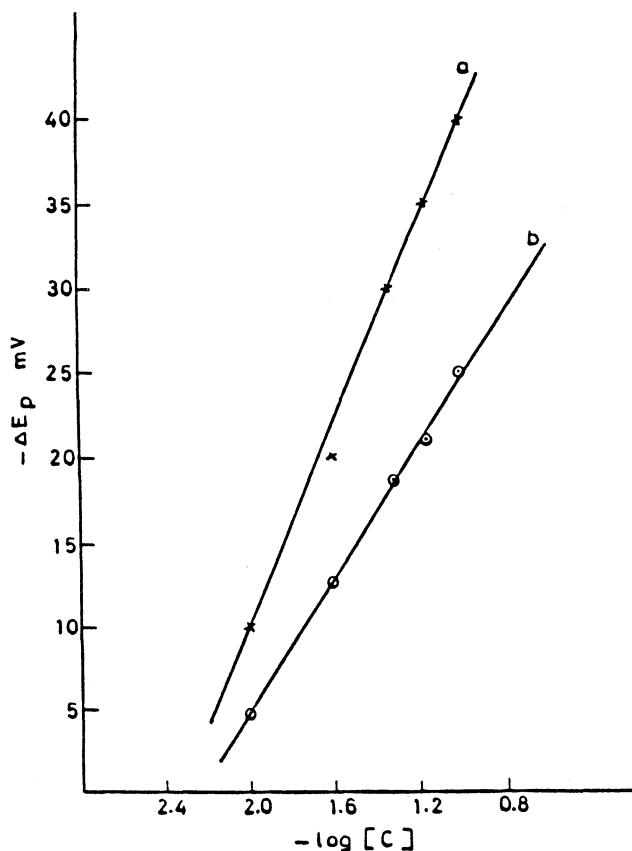


Fig. 2  $E_p$  Vs.  $\log$  [ligand]: (a) for Tl(I)-pyruvate system, (b) for Tl(I)-thiamine system.

The conductometric titration curves of thallium with thiamine or pyruvate exhibit one break at molar ratio 1 : 1 indicating the formation of one type of complexes with stoichiometric ratio 1 : 1 (M : L) which is in accordance with the above results.

**Simultaneous determination of thallium(I), lead(II), selenium(IV), cadmium(II) and copper(II) by using thiamine hydrochloride or pyruvate as complexing agents by a.c. polarography**

The complex formation reaction has been known to provide many useful polarographic methods for the analysis of metal ions. Also in a.c. polarography, it has been reported<sup>25</sup> that, when the difference in the summit potential,  $\Delta E_p$ , of a.c. polarograms is greater than 40 mV, the peak height of each polarogram can be determined accurately.

**(A) Simultaneous determination of thallium, lead, copper, cadmium and selenium in presence of pyruvate.**

The polarographic behaviours of Tl(I), Cu(II), Se(IV), Cd(II) and Pb(II) have been studied using 0.1 M pyruvate (pH 5.44) as supporting electrolyte. Well

defined diffusion-controlled reversible waves for each ion are obtained except Se(IV) do not undergo reduction in this medium. The peak potentials of Tl(I), Pb(II), Cd(II) and Cu(II) are  $-0.52$ ,  $-0.5$ ,  $-0.64$  and  $-0.08$  V respectively.

From these results it is found that we can determine Tl(I), Cu(II) and Cd(II) in presence of each other (Fig. 3) and in presence of selenium without interference (Se(IV) does not undergo reduction in this medium) whereas in the case of lead and thallium, it is found that the peak potentials of each are close together ( $-0.52$  V,  $-0.5$  V for  $Tl^+$  and  $Pb^{2+}$  respectively); therefore, it is difficult to determine simultaneously these metal ions by the polarographic method. However, by adding sodium hydroxide to lead in pyruvate solution to become alkaline medium (pH 12.25) the reduction wave of the lead(II) ions shifts to the negative potential ( $E_p = -0.7$  V) as shown in Fig. 3b. So the resolute determination of thallium(I)

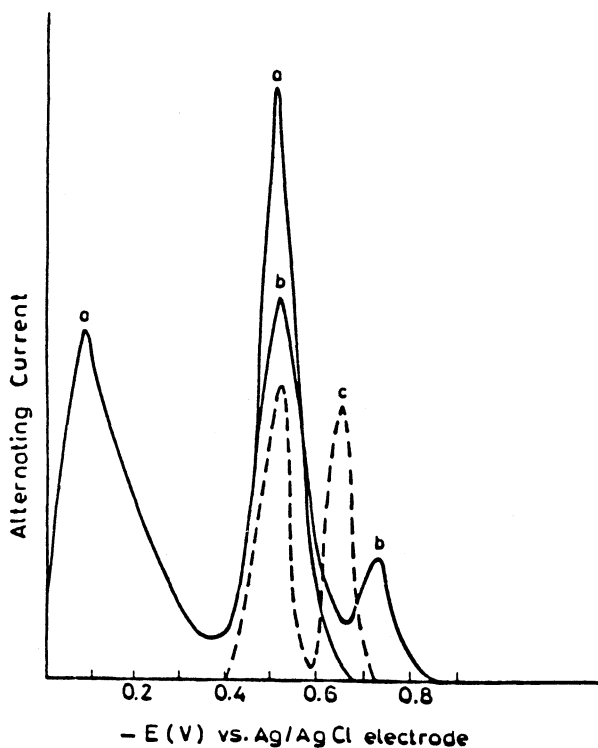


Fig. 3 AC polarograms for Tl(I)-pyruvate system in presence of: (a) 0.5 mM Cu(II), (b) 0.5 mM Pb(II), (c) 0.5 mM Cd(II).

and lead(II) in pyruvate solution (pH 12.25) can be effected successfully. Linear relationships between the reduction currents for Tl(I) (Fig. 4 as representative), Pb(II), Cd(II) and Cu(II) and its concentrations are obtained. The corresponding values of  $I_p/C$  shown in Table 1(a, b, c) within the concentration range applied assume a constant value.

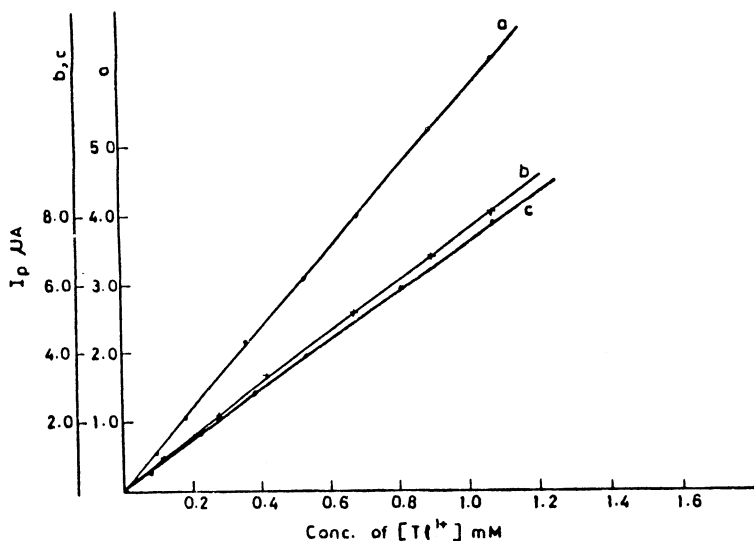


Fig. 4 The  $I_p - C_M$  plots of Tl(I) in presence of 0.1 M pyruvate: (a) in presence of 0.5 mM Pb(II), (b) in presence of 0.5 mM Cd(II), (c) in presence of 0.5 mM Cu(II).

TABLE 1 (a)

POLAROGRAPHIC DETERMINATION OF Tl(I) AND Pb(II) WITH PYRUVATE IN PRESENCE OF EACH OTHER (Pyruvate = 0.1 M, pH = 5.44 for Tl<sup>+</sup> and 12.25 for Pb<sup>2+</sup>)

$C_{Tl^+}$ mM	$I_p$ $\mu A$	$I_p/C$	$C_{Pb^{2+}}$ mM	$I_p$ $\mu A$	$I_p/C$	SD <sup>a</sup>		SE <sup>b</sup>		LD <sup>c</sup> mg/L	
						Tl <sup>+</sup>	Pb <sup>2+</sup>	Tl <sup>+</sup>	Pb <sup>2+</sup>	Tl <sup>+</sup>	Pb <sup>2+</sup>
0.09	0.53	5.86	0.079	0.50	6.33						
0.18	1.05	5.83	0.158	1.00	6.33						
0.36	2.10	5.83	0.234	1.47	6.28						
0.53	3.10	5.85	0.310	1.96	6.32	0.016	0.018	0.006	0.007	0.040	0.032
0.69	4.05	5.87	0.559	3.54	6.33						
0.90	5.25	5.83	1.100	6.93	6.30						
10.8	6.30	5.83									

TABLE 1 (b)

POLAROGRAPHIC DETERMINATION OF Tl(I) AND Cu(II) WITH PYRUVATE IN PRESENCE OF EACH OTHER (Pyruvate = 0.1 M, pH = 5.44)

$C_{Tl^+}$ mM	$I_p$ $\mu A$	$I_p/C$	$C_{Cu^{2+}}$ mM	$I_p$ $\mu A$	$I_p/C$	SD <sup>a</sup>		SE <sup>b</sup>		LD <sup>c</sup> mg/L	
						Tl <sup>+</sup>	Cu <sup>2+</sup>	Tl <sup>+</sup>	Cu <sup>2+</sup>	Tl <sup>+</sup>	Cu <sup>+</sup>
0.08	0.58	7.25	0.132	0.55	3.49						
0.23	1.67	7.26	0.264	0.93	3.52						
0.39	2.83	7.26	0.528	1.85	3.50						
0.53	3.85	7.26	1.180	4.10	3.48	0.009	0.012	0.004	0.005	0.040	0.220
0.81	5.90	7.28	1.830	6.40	3.50						
1.08	7.84	7.26	2.470	8.65	3.50						

a = standard deviation, b = standard error, c = limit of detection.

TABLE 1(c)  
POLAROGRAPHIC DETERMINATION OF Tl(I) AND Cd(II) WITH PYRUVATE IN  
PRESENCE OF EACH OTHER (Pyruvate = 0.1 M, pH = 5.44)

$C_{Tl}$ mM	$I_p$ $\mu A$	$I_p/C$	$C_{Cd^{2+}}$ mM	$I_p$ $\mu A$	$I_p/C$	SD <sup>a</sup>		SE <sup>b</sup>		LD <sup>c</sup> mg/L	
						Tl <sup>+</sup>	Cd <sup>2+</sup>	Tl <sup>+</sup>	Cd <sup>2+</sup>	Tl <sup>+</sup>	Cd <sup>2+</sup>
0.039	0.31	7.60	0.641	0.40	6.24						
0.120	0.91	7.58	0.128	0.80	6.25						
0.270	2.05	7.60	0.191	1.20	6.28						
0.420	3.20	7.60	0.316	1.99	6.30	0.008	0.020	0.003	0.008	0.040	0.055
0.670	5.10	7.60	0.559	3.50	6.26						
0.900	6.84	7.60	1.180	7.35	6.25						
1.080	8.20	7.60									

The standard deviation, standard error and the limit detection are calculated and listed in Table 1(a, b, c).

**(B) Simultaneous determination of thallium, lead, copper, cadmium and selenium in presence of thiamine hydrochloride**

The polarographic behaviours of Tl(I), Cu(II), Se(IV), Cd(II) and Pb(II) have been studied using 0.1 M thiamine hydrochloride (pH 2.2) as supporting electrolyte. A well defined diffusion-controlled reversible waves are obtained, and the summit potentials ( $E_p$ ) of these metal ions are found  $-0.505$ ,  $-0.2$ ,  $-0.62$ ,  $-0.7$  and  $-0.48$  V for Tl(I), Cu(II), Cd(II), Se(IV) and Pb(II) respectively. From the above results it is found that the simultaneous determinations of thallium with copper, cadmium and selenium are possible by sinusoidal a.c. polarography, whereas in the case of lead, it is very difficult to determine simultaneously thallium and lead by this method, because the two metal ions are reduced at potentials very close together, and the summit potentials of the two ions (Tl<sup>+</sup>, Pb<sup>2+</sup>) are unaffected by the addition of surface-active substances such as Triton-X-100, sod. dodecyl benzene sulphonate and gelatin. Also the determination of metal ions at higher pH's (alkaline medium) is not possible owing to the decomposition of thiamine hydrochloride in the alkaline medium.

By adding different concentrations of thallium to the solution of thiamine hydrochloride (0.1 M) containing 0.5 M of copper, cadmium or selenium producing polarograms each consisting of two waves, the peak height of the wave of thallium increases progressively as the concentration of thallium is increased, whereas the peak height of the wave of cadmium, copper or selenium remains unaffected.

The plots  $I_p/C_{Tl^+}$  are straight lines (Fig. 5) passing through the origin. The  $I_p/C_{Tl^+}$  ratios are calculated and listed in Table 2(a, b, c). From the results it is found that the determination of thallium in presence of selenium is quite possible at concentration lower than 0.6 mM of thallium (Fig. 5c). Above this concentration the determination of thallium is not possible.

From the above results it is found that thallium(I) can be determined in presence of Cu(II), Cd(II) and Se(IV) with standard deviation and standard error equal to 0.011 and 0.005 in presence of Cu(II). 0.025 and 0.01 in presence of Cd(II) and



0.981 and 0.4 in presence of Se(IV) respectively; the limit detection of thallium in presence of Cu(II), Cd(II) and Se(IV) is found to be 0.04 mg/L.

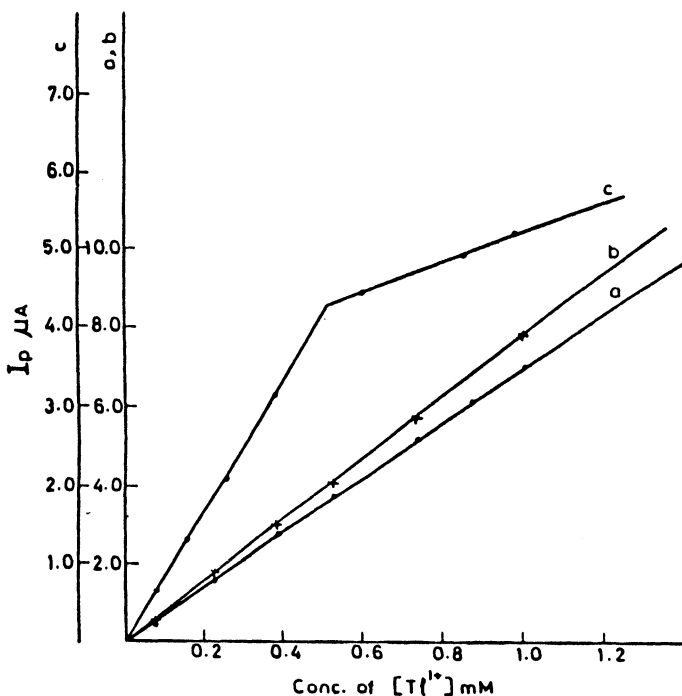


Fig. 5 The  $I_p$ - $C_m$  plots of Tl(I) in presence of 0.1 M thiamine: (a) in presence of 0.5 mM Cu(II), (b) in presence of 0.5 mM Cd(II), (c) in presence of 0.5 mM Se(IV).

TABLE 2 (a)  
POLAROGRAPHIC DETERMINATION OF Tl(I) AND Cu(II) WITH THIAMINE  
HYDROCHLORIDE IN PRESENCE OF EACH OTHER (Thiamine  
hydrochloride = 0.1 M, pH = 2.2)

$C_{Tl^+}$ mM	$I_p$ $\mu A$	$I_p/C$	$C_{Cu^{2+}}$ mM	$I_p$ $\mu A$	$I_p/C$	SD <sup>a</sup>		SE <sup>b</sup>		LD <sup>c</sup> mg/L	
						Tl <sup>+</sup>	Cu <sup>2+</sup>	Tl <sup>+</sup>	Cu <sup>2+</sup>	Tl <sup>+</sup>	Cu <sup>2+</sup>
0.079	0.55	6.96	0.099	0.45	4.55						
0.230	1.60	6.96	0.198	0.90	4.55						
0.390	2.71	6.95	0.279	1.36	4.58						
0.530	3.70	6.98	0.396	1.80	4.55	0.011	0.037	0.005	0.015	0.040	0.190
0.740	5.16	6.97	0.726	3.30	4.55						
0.880	6.12	6.96	0.990	4.60	4.65						
1.010	7.05	6.98	1.320	6.00	4.55						

a = standard deviation, b = standard error, c = limit of detection.

TABLE 2 (b)  
POLAROGRAPHIC DETERMINATION OF Tl(I) AND Cd(II) WITH THIAMINE  
HYDROCHLORIDE IN PRESENCE OF EACH OTHER (Thiamine  
hydrochloride = 0.1, M, pH = 2.2)

$C_{Tl^+}$ mM	$I_p$ $\mu A$	$I_p/C$	$C_{Cd^{2+}}$ mM	$I_p$ $\mu A$	$I_p/C$	SD <sup>a</sup>		SE <sup>b</sup>		LD <sup>c</sup> mg/L	
						Tl <sup>+</sup>	Cu <sup>2+</sup>	Tl <sup>+</sup>	Cu <sup>2+</sup>	Tl <sup>+</sup>	Cu <sup>2+</sup>
0.079	0.60	7.60	0.032	0.20	6.25						
0.230	1.75	7.60	0.064	0.40	6.25						
0.390	2.98	7.64	0.128	0.80	6.25						
0.530	4.05	7.64	0.276	1.74	6.30	0.025	0.029	0.010	0.012	0.040	0.090
0.740	5.65	7.64	0.515	3.20	6.21						
1.010	7.75	7.67	0.640	3.98	6.22						

TABLE 2 (c)  
POLAROGRAPHIC DETERMINATION OF Tl(I) AND Se(IV) WITH THIAMINE  
HYDROCHLORIDE IN PRESENCE OF EACH OTHER (Thiamine  
hydrochloride = 0.1 M, pH = 2.2)

$C_{Tl^+}$ mM	$I_p$ $\mu A$	$I_p/C$	$C_{Se^{4+}}$ mM	$I_p$ $\mu A$	$I_p/C$	SD <sup>a</sup>		SE <sup>b</sup>		LD <sup>c</sup> mg/L	
						Tl <sup>+</sup>	Se <sup>4+</sup>	Tl <sup>+</sup>	Se <sup>4+</sup>	Tl <sup>+</sup>	Se <sup>4+</sup>
0.079	0.63	7.97	0.088	0.30	3.4						
0.160	1.27	7.94	0.260	0.86	3.3						
0.260	2.07	7.96	0.550	1.80	3.3						
0.390	3.10	7.95	0.800	2.64	3.3	0.981	0.019	0.400	0.0085	0.040	0.063
0.600	4.00	7.33	1.360	4.50	3.3						
0.860	5.76	6.70	—	—	—						
0.990	5.20	5.25	—	—	—						

a = standard deviation, b = standard error, c = limit of detection

Furthermore, determinations of Cu(II), Cd(II) and Se(IV) in presence of 0.5 mM of thallium(I) are investigated, the results obtained are recorded in Table 2 (a, b, c). From these results it is found that the standard deviation, standard error; and limit of detection are 0.037, 0.015 and 0.19 mg/L for copper, 0.029, 0.012 and 0.09 mg/L for cadmium and 0.019, 0.0085 and 0.063 mg/L for selenium respectively.

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(Received: 11 May 1992; Accepted: 8 March 1993)

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