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## SYNTHESIS AND CHARACTERIZATION OF NEW SCHIFF BASES AND THEIR COMPLEXATION WITH LEAD (II) AND TELLURIUM (IV) ELECTROCHEMICAL STUDY

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### ABSTRACT

Schiff bases, resacetophenone imines [RPT] ligand was synthesized by using Tris (Hydroxymethyl) methylamine (TRIS) and resacetophenone and has not been used so far for the determination of Lead and Tellurium in trace quantities. Effect of pH on wave height for Pb-[RPT] and Te-[RPT] systems have been studied at pH 6.5–11.0 in 0.1 M NaNO<sub>3</sub>, and 0.002 % Triton-X-100 which increases the stability of the complex. Effects of Ligand concentrations, height of mercury column, metal ion concentrations on Lead and Tellurium on wave height at pH 10.0 have been studied. The author also investigates metal–ligand ratio and stability constants of Tellurium–RPT by reversible system.

**Key words:** Polarographic, Schiff Base, Lead, Tellurium And Lingane Method.

### INTRODUCTION

Many number of Schiff bases were synthesized from Tris (Hydroxymethyl) methylamine with different aldehydes and were tested as pharmaceutical intermediates [1-2]. Schiff bases prepared by Inoyatov[3] act as effective polymers. Spectrophotometric work [4] on the azomethine of pyridoxal- 5'-phosphate-Tris was carried out and determined the formation constant (pKa) values. Patel<sup>5</sup> reported polarographic determination of ligand–proton stability constants for Salicylaldehyde–Tris (ST) Schiff base in 50% DMF. Effect of pH, amine concentration and solution composition of pyridoxal-5'-phosphate–Tris was reported by Sevilla,J.M[6] employing polarographic technique, Sreenivasulu[7] reported the effect of pH, supporting electrolytes, solvents

and acid concentration on the polarographic reduction of ST. Characterization of seven new Schiff bases derived from Tris and various aldehydes was reported [8-12] and determine metal –ligand ratio and stability constants of complexes of Tellurium(II) and Lead(II) in presence of Schiff bases derived from Tris and various ketones in KNO<sub>3</sub> as supporting electrolyte at pH 10.5 in 50% DMF–water medium.

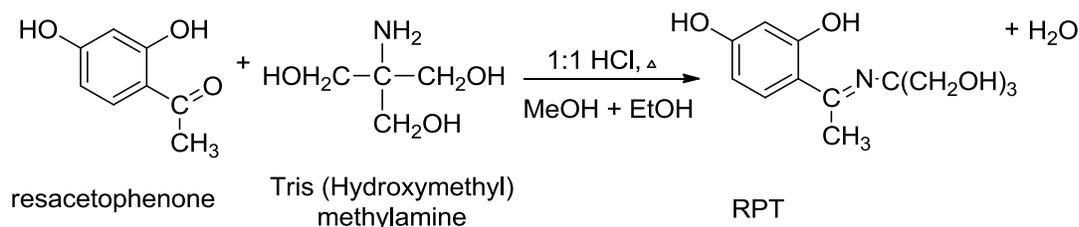
The author has been developed polarographic methods for the determination of Pb(II) and Te(IV) using RPT as complexing agent in NaNO<sub>3</sub> as the supporting electrolyte at pH 10.0 in methanol–water medium (40 : 60). The studies include effect of pH, effect of ligand concentration, effect of height of mercury column and effect of metal ion concentration. The studies were aimed at establishing the complexing ability of 1–[2,4–dihydroxy phenyl] ethanone–Tris and developing a procedure for the determination of various metal ions present individually and in binary mixtures constituting important alloys and ores of industrial importance.

## EXPERIMENTAL

### Preparation and Characterization of resacetophenone imines [RPT] Ligand:

#### Preparation of the ligand

Equimolar concentrations of Tris (Hydroxymethyl) methylamine (TRIS) and 1–[2,4–dihydroxy phenyl] ethanone were dissolved separately in methanol and refluxed for one hour in methanol & ethanol solvent mixture in presence of few drops of acid catalyst namely SOCl<sub>2</sub>. The refluxed solution was allowed to cool and kept aside for overnight. White crystalline needles were obtained and the compound was recrystallized. The melting point and yield of the compound were found to be 133–134°C and 74% respectively.



#### Characterization of the ligand

The characterization of the Schiff base was made by Elemental analysis, Chemical reactions and IR studies. Elemental analysis for Carbon, Hydrogen, Oxygen and Nitrogen present in the Schiff base was obtained from CDRI, Lucknow, India. Chemical analysis for the functional groups i.e., carbonyl (>C=O) and amine (–NH<sub>2</sub>) groups was carried out by standard procedure and found to be absent indicating the formation of azomethine.

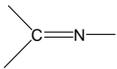
An infrared spectrum for the derived Schiff base was recorded by KBr Pallet method employing Perkin Elmer IR spectroscopy. The Infrared spectrum of the compound (RPT) formed between Tris( hydroxymethyl) methyl amine and resacetophenone showed peak at 1630 cm<sup>-1</sup> indicating the existence of >C=N– group in the compound. The Peaks were also observed in the region of 3340 – 3330 cm<sup>-1</sup> (broad, strong, OH–stretching), 3190–3180 cm<sup>-1</sup> (broad, medium, phenolic OH),

1600, 1580, 1500, 1480  $\text{cm}^{-1}$  (aromatic  $>\text{C}=\text{C}<$  vibrations) and 1220  $\text{cm}^{-1}$  (small, medium,  $>\text{C}=\text{O}$  stretching coupled phenolic – OH deformation). The above IR data clearly suggested that the chemical reaction between the amino group of Tris and the carbonyl group of resacetophenone resulting in the formation of respective Schiff base compound. The elemental analysis and IR data were tabulated in the (Table 1).

### NMR spectra

In the present investigation  $^1\text{H}$  NMR spectrum was obtained for the ligand RPT using Gemini – 200MHz  $^1\text{H}$  NMR Spectrometer from IICT, Hyderabad, in  $\text{DMSO}-\text{D}^6$  solvent at room temperature. Important chemical shift values for various protons such as methyl proton attached to azomethine group, methyl protons of hydroxy methyl group, hydroxyl protons of hydroxy methyl group, hydroxyl protons of aromatic hydroxy group and aromatic protons present in the compound were summarized in the (Table 2).

**Table 1:** Analytical and IR spectral data of [RPT] Ligand

<b>Molecular Formula</b>	$\text{C}_{12}\text{H}_{17}\text{NO}_5$	
<b>Colour</b>	White crystalline needles	
<b>Melting point</b>	133 – 134 $^\circ\text{C}$	
<b>Elemental analysis</b>	<b>Found (%)</b>	<b>Calc. (%)</b>
Carbon	56.45	56.46
Hydrogen	6.69	6.71
Oxygen	31.32	31.34
Nitrogen	5.48	5.49
<b>Yield</b>	74%	
<b>IR absorption band</b>	1630 $\text{cm}^{-1}$	
		

**Table 2:**  $^1\text{H}$ - NMR spectral data for [RPT] Ligand in  $\text{DMSO}-\text{D}^6$

Sl. No.	Different protons in the Ligand	Chemical shift ( $\delta$ ) in ppm
1	$\text{H}_3\text{C}-\text{C}=\text{N}$ (methyl protons attached to azomethine group)	3.38
2	$-\text{CH}_2\text{OH}$ (Methyl protons of hydroxymethyl group)	3.80
3	$-\text{CH}_2\text{OH}$	4.57

	(Hydroxyl protons of hydroxymethyl group)	
4	Ar-OH (Hydroxyl Protons of Aromatic hydroxy group)	5.91
5	Aromatic protons	6.52 – 7.61

## RESULTS AND DISCUSSION

### Polarographic Behavior of Individual Metal Ions ( $\text{Pb}^{2+}$ , $\text{Te}^{4+}$ ) in Presence of [RPT]

#### a) Effect of pH on the Wave height

The main purpose of studying effect of hydrogen ion concentration on polarographic wave is to ascertain the hydrogen ion participation in electrochemical reduction at d.m.e. Further, it is also useful to fix an appropriate pH value at which separation of two or more metal ions is possible present in mixture solutions. In the present study, effect of pH on various metal ions in presence of 0.1M  $\text{NaNO}_3$  as the supporting electrolyte at 0.1M ligand concentration at mercury height of 70.0 cms in 40 : 60 methanol- water medium. The pH range studied for Lead and Tellurium was between 6.5–11.0. From  $E_{3/4} - E_{1/4}$  value computed from the polarograms of pH studies indicated that, Lead and Tellurium reduced reversibly as shown in (Table 3&4) respectively.

**Table.3:** Effect of pH on Lead – [RPT] system

pH	$E_{1/2}$	$E_{3/4} - E_{1/4}$
	(-V. Vs S.C.E)	(mV)
6.5	0.442	28.06
8.0	0.479	28.02
9.0	0.524	27.14
10.0	0.596	26.22
11.0	0.674	26.32

**Note:**  $[\text{Pb}^{2+}] = 1.0 \text{ mM}$ ,  $[\text{RPT}] = 0.1 \text{ M}$ ,  $[\text{NaNO}_3] = 0.1 \text{ M}$ , Triton -x-100=0.002%.

**Table 4:** Effect of pH on Tellurium – [RPT] system

pH	$E_{1/2}$	$E_{3/4} - E_{1/4}$
	(-V. Vs S.C.E)	(mV)
6.5	0.835	37.20

8.0	0.854	35.16
9.0	0.930	28.96
10.0	1.029	28.90
11.0	1.048	22.76
<b>Note:</b> [Te <sup>4+</sup> ]=1.0 mM, [RPT]=0.1M, [NaNO <sub>3</sub> ]=0.1M, Triton -X-100=0.002%		

### Effect of Ligand concentration

Effect of ligand concentration on polarographic wave is of considerable importance since; it gives whether the polarographic wave is controlled by diffusion alone or depends on some other factors such as kinetic, adsorption or catalytic currents. Further, it also helps to establish the validity of Ilkovic equation. Well defined polarograms obtained with different concentrations of the ligand enables to carryout qualitative determination of metal ions in binary, ternary etc. mixtures constituting important ores and alloys. In addition to the above application, the studies also help to establish the complexation of ligand with various metal ions. In view of the above advantages, the author in the present investigations studied effect of varying concentrations of the RPT ligand on Lead (II) and Tellurium (IV) in the presence of 0.1 M NaNO<sub>3</sub> as supporting electrolyte and 0.002% of Triton-X-100 as maximum suppressor at pH 10.0. The results indicated that RPT was able to complex with Lead and Tellurium ions under consideration by the fact that diffusion current ( $i_d$ ) decreased whereas half-wave potential ( $E_{1/2}$ ) shifted towards more negative values with increasing concentration of the ligand as shown in (Figure 1-4) and (Table 5&6). Further, the studies also suggested that Lead and Tellurium reduced reversibly at d.m.e.

**Table 5:** Effect of Ligand - [RPT] concentration on Lead

[RPT]	$E_{1/2}$	$i_d$	Slope
(M)	(-V. Vs S.C.E)	( $\mu$ A)	(mV)
0.04	0.585	5.7775	31.82
0.06	0.590	5.4766	31.78
0.08	0.594	5.1762	30.36
0.10	0.596	5.0805	30.34
0.20	0.604	4.7972	29.88
0.40	0.610	4.3065	29.88
0.60	0.618	3.9261	28.78
0.80	0.621	3.4940	28.58
1.00	0.624	2.9278	28.58

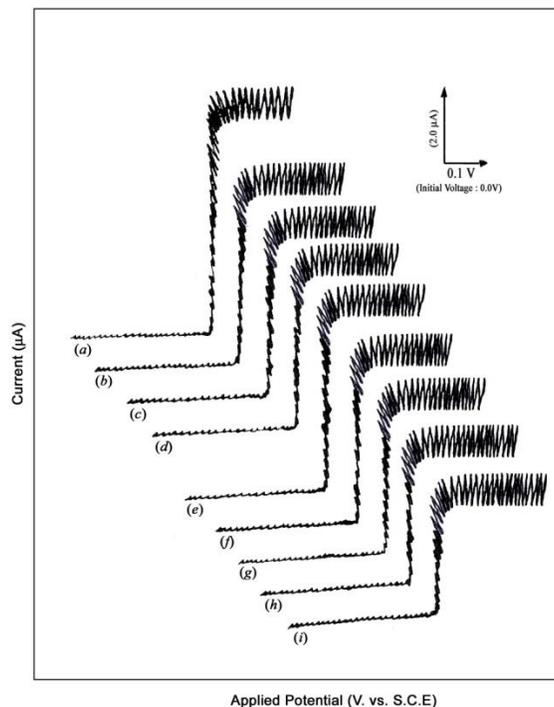


Figure 1: Polarograms of 0.2 mM Lead ion in a) 0.04 b) 0.06 c) 0.08 d) 0.10 e) 0.20 f) 0.40 g) 0.60 h) 0.80 i) 1.00 M [RPT] and 0.1M NaNO<sub>3</sub> at pH 10.0.

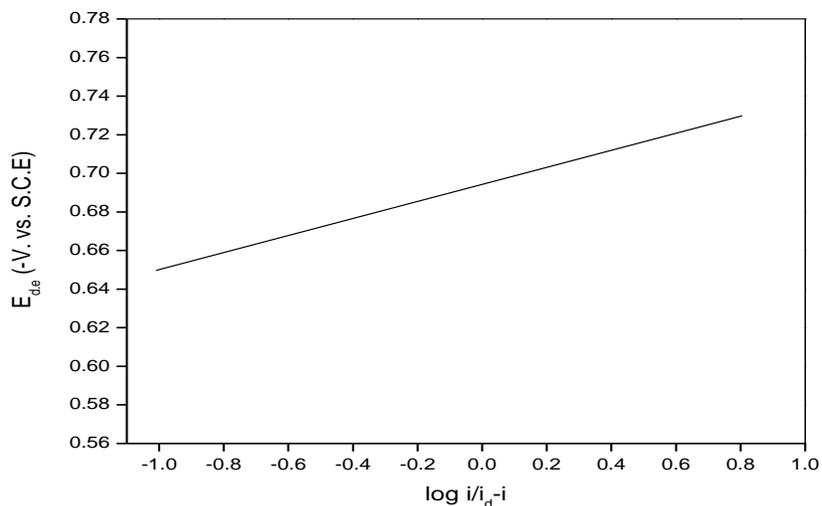


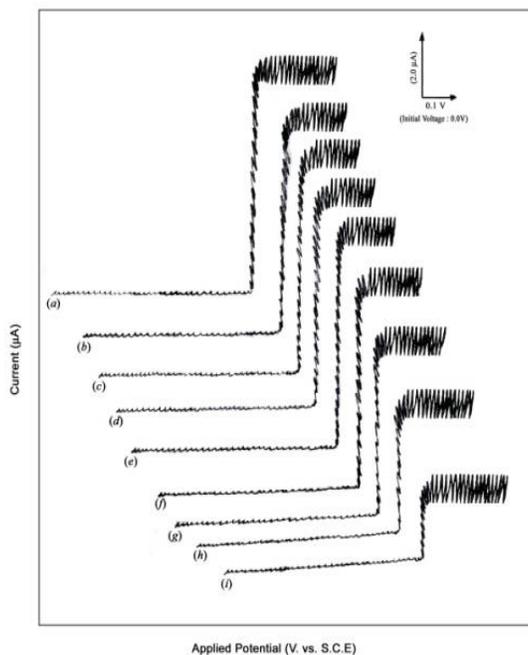
Figure 2: A typical log plot of 1.0 mM Lead in 0.1 M [RPT] and 0.1M NaNO<sub>3</sub> at pH 10.0.

Table.6: Effect of Ligand- [RPT] concentration on Tellurium

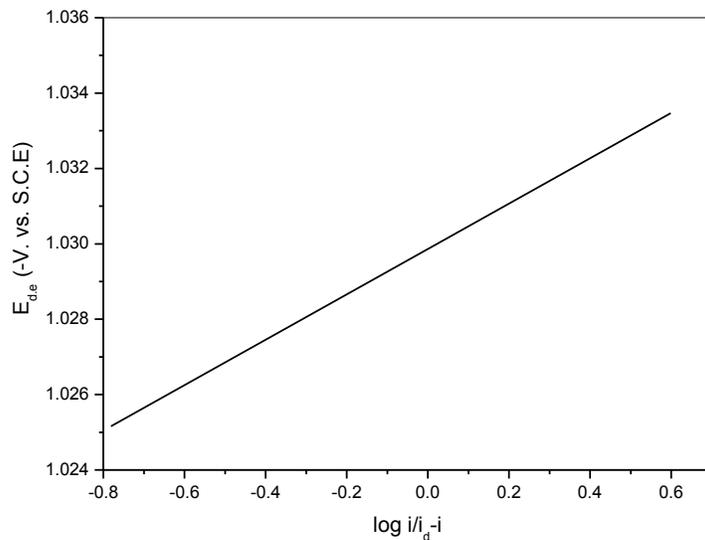
[RPT]	E <sub>1/2</sub>	i <sub>d</sub>	Slope
(M)	(-V. Vs S.C.E)	(µA)	(mV)

0.04	1.025	13.2945	32.38
0.06	1.026	12.4549	32.58
0.08	1.028	12.3546	32.64
0.10	1.029	12.3448	30.34
0.20	1.030	12.1075	30.54
0.40	1.032	11.3952	29.92
0.60	1.034	9.4960	26.36
0.80	1.036	7.1220	26.32
1.00	1.038	3.7984	28.04

**Note:** [Te<sup>4+</sup>] = 1.0 mM, [NaNO<sub>3</sub>] = 0.1M, pH = 10.0, Triton -x-100 = 0.002%.



**Figure 3:** Polarograms of 1.0 mM Tellurium ion in a) 0.04 b) 0.06 c) 0.08 d) 0.10 e) 0.20 f) 0.40 g) 0.60 h) 0.80 i) 1.00 M [RPT] and 0.1M NaNO<sub>3</sub> at pH 10.0.



**Figure 4:** A typical log plot of 1.0 mM Tellurium in 0.1 M [RPT] and 0.1M NaNO<sub>3</sub> at pH 10.0.

### ***Effect of height of mercury column***

Effect of height of mercury column on polarographic wave helps to establish the diffusion controlled nature of the electrode reaction at d.m.e by calculating  $i_d/\sqrt{h}$  values. In the present studies, the author investigated in detail the influence of mercury height on diffusion current of metal ions such as Lead(II), Tellurium(IV) ions at 1.0 mM concentration in presence of fixed concentration of RPT ligand (0.1M), ionic concentration 0.1M NaNO<sub>3</sub> as supporting electrolyte and 0.002% of Triton-X-100 as maximum suppressor at pH 10.0. Results indicated that  $i_d/\sqrt{h}$  values were constant within the experimental error. (Tables 7,8) indicates that the diffusion controlled nature of both the metal ions under consideration at d.m.e. Mercury height of 70.0 cms was fixed to carry out other studies like effect of pH effect of ligand concentration and effect of metal ion concentration.

**Table 7:** Effect of height of Mercury Column on Lead – [RPT] system.

Height of Mercury Column	$i_d$	$i_d/\sqrt{h}$
h(cm)	( $\mu$ A)	
80	5.4573	0.6101
75	5.2944	0.6113
70	5.0805	0.6072
65	4.8879	0.6061
60	4.7242	0.6098
<b>Note:</b> [Pb <sup>2+</sup> ]=1.0 mM, [RPT]=0.1M, [NaNO <sub>3</sub> ]=0.1M, pH=10.0, Triton -x-100=0.002%		

**Table 8:** Effect of height of Mercury Column on Tellurium – [RPT] system

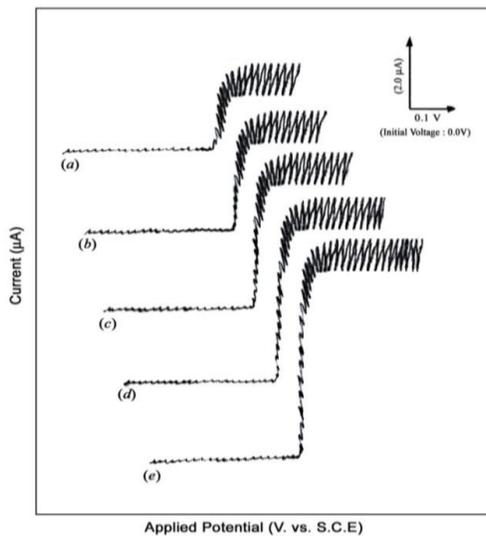
Height of Mercury Column	$i_d$	$i_d/\sqrt{h}$
h(cm)	( $\mu$ A)	
80	13.1965	1.4754
75	12.7892	1.4767
70	12.3448	1.4755
65	11.8931	1.4751
60	11.4288	1.4754
<b>Note:</b> [Te <sup>4+</sup> ]=1.0 mM, [RPT]=0.1M, [NaNO <sub>3</sub> ]=0.1M, pH=10.0, Triton -x-100=0.002%		

### Effect of metal ion concentration

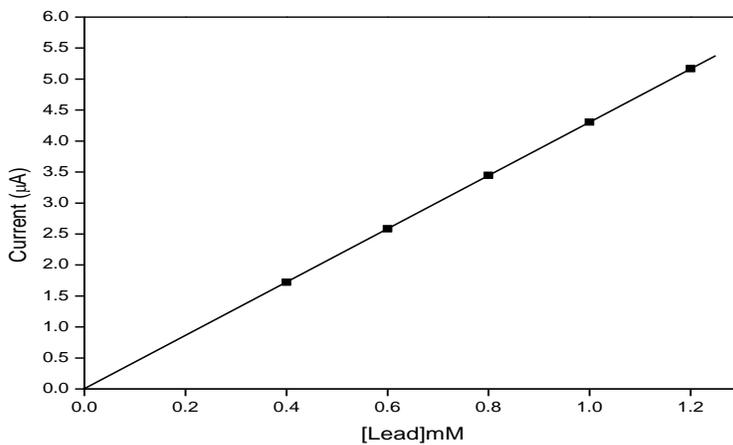
The studies of effect of metal ion concentration on polarographic wave height are of immense importance due to the fact that it establishes diffusion controlled nature of the electrode reaction and the validity of Ilkovic equation. Further, the studies also help us to carryout quantitative determination of metal ions by constructing calibration plots at different concentrations of the depolarizer. In the present investigations, the carried out Polarographic studies Fig 5 and 7 of Lead and Tellurium metal ions of biological and industrial importance. Metal ion concentration was varied from 0.4 mM to 1.2 mM in presence of complexing agent RPT (0.2M), 0.1M NaNO<sub>3</sub> as supporting electrolyte and 0.002% of Triton-X-100 at pH 10.0. Calibration graphs were drawn at different concentrations of metal ion under identical conditions as shown in Fig-6 and 8. In all the instances, straight line plots were obtained passing through the origin indicating the validity of Ilkovic equation. Values computed for  $i_d/c$  were constant within the experimental error was shown in (Table 9,10). The metal ions whose half-wave potential difference was more than 0.2 V were selected to carry out quantitative analysis present in binary mixtures constituting different important ores and alloys.

**Table.9:** Effect of Lead ion concentration on the Wave height.

[Pb <sup>2+</sup> ]	$i_d$	$i_d/c$
(mM)	( $\mu$ A)	
0.4	1.7221	4.7970
0.6	2.5839	4.7974
0.8	3.4458	4.7971
1.0	4.7972	4.7975
1.2	5.1679	4.7973
<b>Note:</b> [RPT]=0.2M, [NaNO <sub>3</sub> ]=0.1M, pH=10.0, Triton -X-100=0.002%		



**Figure 5:** Polarograms of a) 0.4 b) 0.6 c) 0.8 d) 1.0 and e) 1.2 mM Lead in 0.2 M [RPT] and 0.1M NaNO<sub>3</sub> at pH10.0.

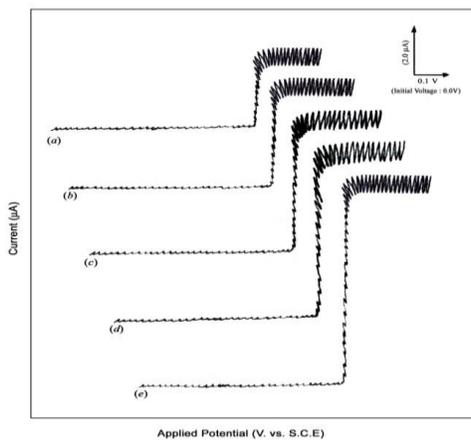


**Figure 6 :** Calibration Plot of Lead ion in 0.2M ligand [RPT] and 0.1M NaNO<sub>3</sub> at pH 10.0.

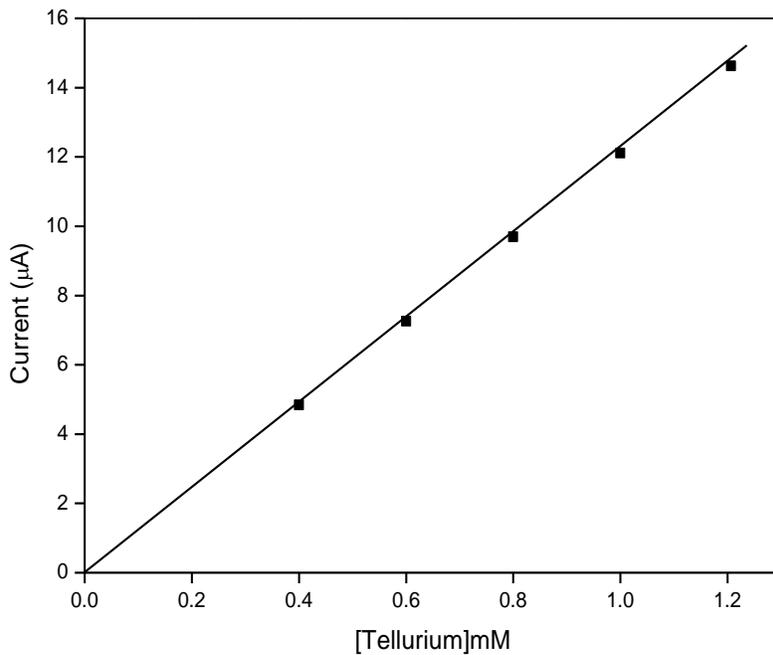
**Table 10:** Effect of Tellurium ion concentration on the Wave height

[Te <sup>4+</sup> ] (mM)	i <sub>d</sub> (µA)	i <sub>d</sub> /c
0.4	4.8387	
0.6	7.2629	12.1048
0.8	9.6937	12.1171

1.0	12.1075	12.1075
1.2	14.5292	12.1076
<b>Note:</b> [RPT]=0.2M, [NaNO <sub>3</sub> ]=0.1M, pH=10.0, Triton -X-100=0.002%		



**Figure 7 :** Polarograms of a) 0.4 b) 0.6 c) 0.8 d) 1.0 and e) 1.2 mM Tellurium in 0.2 M [RPT] and 0.1M NaNO<sub>3</sub> at pH 10.0.



**Figure 8:** Calibration Plot of Tellurium ion in 0.2M ligand [RPT] and 0.1M NaNO<sub>3</sub> at pH 10.0

*Investigation of metal–to–ligand ratio and stability constants of Tellurium – RPT reversible system*

Earlier polarographic investigation on Tellurium in presence of complexing agent RPT. 0.1M NaNO<sub>3</sub> as supporting electrolyte and 0.002% of Triton-X-100 as maximum suppressor at pH 10.0 revealed that Tellurium undergone reversible electrode reaction at d.m.e. The graph plotted against  $E_{1/2}$  and  $-\log [RPT]$  gave a smooth curve showing the existence of various step-wise complex equilibria in solution. The author, therefore, prepared the solution in 40: 60 Methanol: water medium. Lingane method was therefore, adopted for the determination of metal-to-ligand ratio and stability constant of Lead-RPT complex using the following equation

$$\Delta E_{1/2} = \frac{0.0591}{n} \log \beta_{m \times J} + J \frac{0.059}{n} \log [X]$$

Where the symbols represent their usual significance. The coordination number (J) was determined by equating the slope A the plot to  $J \frac{0.059}{n}$  where 'n' representing number of participating in the electrode reaction. The ligand number obtained from the slope 'A' the graph was found to be two. Further, the stability constant of Lead-RPT system calculated at 1.0M concentration to the ligand RPT was equal to  $\beta_{m \times J} = 8.2943 \times 10^7$ . Experimental results were reported in the (Table 11).

**Table 11:** Effect of Ligand concentration on Lead – [RPT] System

[RPT] (M)	$E_{1/2}$ (-V. vs S.C.E)	$i_d$ ( $\mu$ A)	Slope (mV)	log [RPT]
0.00	0.390	6.0680	28.32	–
0.02	0.576	5.9228	31.82	–1.6989
0.04	0.585	5.7775	31.82	–1.3979
0.06	0.590	5.4766	31.78	–1.2218
0.08	0.594	5.1762	30.36	–1.0969
0.10	0.596	5.0805	30.34	–1.0000
0.20	0.604	4.7972	29.88	–0.6989
0.40	0.610	4.3065	29.88	–0.3979
0.60	0.618	3.9261	28.78	–0.2218
0.80	0.621	3.4940	28.58	–0.0969
1.00	0.624	2.9278	28.58	–0.0000

## CONCLUSIONS

Determination of traces quantities of Lead(II) and Tellurium(IV) using RPT Schiff base by polarographic method is not tedious and do not involve any heating, separation or extraction of the components. Determination of metal ions Lead and

Tellurium using RPT ligand is simple and selective and rapid, can be applicable in determinations in metallurgy, environmental analysis (air, water, and sea water contaminants), Food analysis, analysis of drugs, pharmaceutical preparations and determination of pesticide or herbicide residues in the foods and other samples.

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