

Polarographic Estimation of Silver and Selenium in Soil Samples Adjacent to Khetri Copper Mines in Presence of 2,3-Dihydroxy Pyridine

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Polarographic estimation of silver and selenium in eight different soil samples collected in the vicinity of Khetri Copper Project, Rajasthan, have been reported using 2,3-dihydroxy pyridine as a complexing agent.

INTRODUCTION

Due to the importance of the presence of silver and selenium in different sites adjoining Khetri Copper Project, an attempt for polarographic estimation of these two elements is reported. A procedure for such determination is recommended and the effect of mercury pressure, 2,3-dihydroxy pyridine (DHP) concentration, pH and foreign ion concentration has been discussed. Mixed polarograms and simultaneous determination are studied. A survey of literature reveals that the polarographic determination of Yb¹ and the stability constants of Tl², In³ and Eu⁴ complexes with 2,3-dihydroxy pyridine have been reported. The results of our investigation are very promising and are reproduced here.

EXPERIMENTAL

Reagents used were analytical grade; solutions of the metals were prepared by dissolving appropriate salts of silver and selenium in solvent in which these are soluble and standardized by conventional method in double distilled water. Potassium nitrate solution was used to keep the ionic strength constant at 0.1 M. Gelatin solution (0.002%) was used to eliminate the polarographic maxima. Ammonia/ammonium chloride buffer was prepared. Triple distilled mercury was used for dropping mercury electrode (DME).

The capillary characteristics of DME were $m = 2.514 \text{ mg/s}$, $t = 5 \text{ s m}^{3/2}$, $t^{1/6} = 2.415$ or $2.42 \text{ mg}^{2/3} \text{ s}^{-1/2}$ at $h = 50 \text{ cm}$ in 0.1 M potassium nitrate solution (in open circuit). The polarogram is recorded at $25 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

Effect of pH: The polarograms of the solution containing 1 mM of Ag(I) and Se(II) were recorded using manually operated polarograph (Osaw slide wire

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potentiometer and galvanometer AJCO, model No. P-GI, Sr. No. P 71049) having sensitivity of $3.71 \times 10^{-2} \mu\text{A}/\text{div}$ and H-type well saturated with sodium chloride agar agar bridge and 2,3-dihydroxy pyridine (0.1 mM), at various pH values, and a well defined wave was obtained in the pH range 10.0 to 11.4. The diffusion current did not change in this pH range. Hence, this pH range was chosen to study the polarographic behaviour of these soil samples metal-DHP complexes.

Effect of mercury pressure: Polarograms of the respective metal ion (0.01 mm) and DHP solution (0.1 m) were recorded at various heights of the mercury column. The linear dependence of the limiting current on the square root of the mercury column indicated that the rate of reduction of the metal-DHP complex was a diffusion controlled process.

Effect of DHP: The shape of the wave did not change when the DHP was increased from 1 to 4 mM. The formation of the complex was evident as the half wave potential became more negative with increasing concentration of DHP (Table-1). The value of diffusion current for reduction of metal ions in the presence of ligand was smaller than in its absence, proving larger size of the complexed ion. The plot of $\log i/(i_d - i)$ vs. E_{de} (potential of the dropping electrode) is a straight line for all the three systems. The values of the slopes and half wave potentials for various concentrations of DHP are given in Table-1. The slopes of semi log plots reveal that two-electron reversible reduction took place in the case of Ag-DHP and Se-DHP complexes.

TABLE-1
EFFECT OF LIGAND CONCENTRATION IN Ag(I) AND Se(II)
DHP-COMPLEX SYSTEMS

[Ag(I)], [Se(II)] = 0.1 mM, $\mu = 0.1$ M KNO_3 , mercury at 50 cm height, pH ($\text{NH}_3/\text{NH}_4\text{Cl}$ buffer) = 10.0, maximum suppresser = 0.002% gelatin

DHP (mm)	i_d (μA)	$E_{1,2}$ (V vs. SCE)	Slope of the log plot
Ag(I)-DHP System			
0	1.20	0.220	31
1	0.65	0.230	29
2	0.60	0.230	30
3	0.60	0.245	29
4	0.60	0.245	31
Se(II)-DHP System			
0	1.00	0.315	29
1	0.60	0.385	31
2	0.60	0.440	30
3	0.70	0.480	30
4	0.60	0.590	31

Effect of metal ion concentration: Polarograms over the concentration ranges 0.10–0.30 mM of silver (Ag^+) and 0.05–0.25 mM of Se^{2+} were recorded in the presence of 1 mM of DHP, 0.1 M potassium nitrate and 0.002% gelatin of pH 10.0. The diffusion currents were measured by the extrapolation method and

calibration curves constructed. The diffusion current increased linearly in each case which confirmed that waves were diffusion controlled. Hence the polarographic results can be used for their qualitative determination.

Recommended procedure for the determination of Ag(I) and Se(II)

Calibration curve was prepared for each metal by recording the polarograms of the metal at various concentrations. The diffusion current values of the polarograms were plotted against the concentration of the metal ion. To determine the metal ion content in an unknown solution, polarogram was recorded under identical conditions.

The diffusion current value was obtained and the corresponding concentration of the metal ion in the solution was determined from the linear calibration plot. The results are given in Table-2.

TABLE-2
POLAROGRAPHIC DETERMINATION OF Ag(I) AND Se(II)
WITH DHP

[DHP] = mM, μ = 0.1 M KNO₃, h = 50 cm,
pH (NH₃/NH₄Cl buffer) = 10.0,
maximum suppresser = 0.002% gelatin

Metal	Amount of metal (mg)	
	Taken	Found
Ag	0.068	0.066
	0.121	0.120
	0.145	0.145
	0.187	0.185
Se	0.241	0.238
	0.365	0.359
	0.394	0.392
	0.414	0.412

Effect of foreign ions

The effect of various anions and cations at a fixed concentration of silver and selenium (1 mM) with 0.1 M DHP were ascertained. In the presence of nitrate, sulphate, acetate and formate, the half wave potential values remained almost constant in all cases. Out of the metal ions examined only Cu(II), Pd(II) and Zn(II) interfere while Cd(II), Zn(II) and Mn(I) did not interfere up to fifteenfold axes in the polarographic determination of Ag(I) and Se(II).

Mixed polarograms of Ag(I) and Se(II)

From the individual polarograms of Ag(I) and Se(II), it is possible to differentiate the two metal ions in the DHP solution as their half wave potentials differed by more than 0.8 V. Consequently, a series of polarograms were recorded with mixed solutions of the two metal ions and the diffusion current values measured for each metal ion were referred to the respective calibration curves and the metal ion concentration was calculated (Table-3).

TABLE-3
SIMULTANEOUS POLAROGRAPHIC DETERMINATION OF Ag(I) AND Se(II)
WITH DHP

[DHP] = 1 mM, μ = 0.1 M KNO₃, h = 50 cm., pH (NH₃/NH₄Cl buffer) = 10.0,
maximum suppresser = 0.002% gelatin

Amount of metal added (mg)		Amount of Metal found (mg)	
Ag	Se	Ag	Se
0.124	0.045	0.120	0.041
0.248	0.151	0.244	0.149
0.369	0.168	0.361	0.170
0.394	0.226	0.390	0.221

Determination of Ag in ore

The proposed method was applied for estimation of silver in ore samples collected from the vicinity of Khetri Copper Complex, Rajasthan. A powdered sample (0.1 g) of the ore was mixed with 5% bromine solution (10 mL) in CCl₄. The beaker was covered and after 1 h concentrated HNO₃ was added and the mixture was allowed to stand at room temperature overnight.

Bromine and CCl₄ were removed by gentle heating, then cooled and 50% (v/v) H₂SO₄ (5 mL) and HF (20 mL) were added and the solution was allowed to evaporate to dryness to ensure removal of HF. After cooling, aqua regia (20 mL) was added and heated gently on a hot plate at ca. 60°C for 1 h. The volume was then reduced to about 10 mL and the solution was filtered and the filtrate was made up to 100 mL. The solution (1 mL) used in the determination contained about 0.15 mg of Ag. The results are given in Table-4.

TABLE-4
POLAROGRAPHIC DETERMINATION OF Ag(I) AND Se(II) IN THE SOIL
ORE SAMPLE

Found value (%) Ag	Mean value (%) Ag	Accepted value	Standard deviation	Error (%)
1.84				
1.76				
1.51	1.59	1.50	+0.09	0.11
1.02				
1.86				
Found value (%) Se	Mean value (%) Se	Accepted value	Standard deviation	Error (%)
0.99				
0.86				
0.92	0.69	0.64	+0.05	0.16
0.07				
0.65				

Simultaneous determination of Ag(I) and Se(II) in soil ore samples

The present method was successfully applied for the simultaneous determination of Ag(I) and Se(II) in soil ore samples collected from the vicinity of Khetri Copper Mine, Rajasthan. The method for the decomposition of ore was exactly the same as stated before. The results obtained are given in Table-5.

TABLE-5
SIMULTANEOUS POLAROGRAPHIC DETERMINATION OF Ag(I) AND Se(II) IN SOIL ORE SAMPLE

Value found (%)		Mean Value (%)		Accepted Value (%)	
Ag	Se	Ag	Se	Ag	Se
1.32	0.248				
1.13	0.113				
1.01	0.194	1.17	0.185	1.10	0.179
1.16	0.200				
1.23	0.173				

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REFERENCES

1. R.S. Sindhu, S.K. Bansal, S. Tikku and S. Shrey, *Trans. SAEST*, **24**, 219 (1989).
2. R.S. Sindhu, *Trans. SAEST*, **21**, 85 (1986).
3. R.S. Sindhu, K.B. Pandeya and R.P. Singh, *Monatsh. Chem.*, **108**, 361 (1977).
4. R.S. Sindhu and R.P. Singh, *Rev. Roum. Chim.*, **30**, 581 (1985).

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