Report of the minor UGC project

entitled

Spectrophotometric study of complexes by Job’s method

By

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Introduction

Jobs Method of Continuous Variation

A number of methods are used to determine the formulae and stability constant of complexes spectrophotometrically, out of which one is the method of continuous variation, which was designed by Job, hence called as job's method.

The principle of continuous variation was employed by ostromisslensky in 1911 to establish the 1:1 stoichiometry of the adduct formed between nitrobenzene and aniline. However the principle was then applied by job in the study of formation of complexes of coordination compounds and hence named after him as jobs method. Job assumed that only one complex is present in solution. The method is also described in another way which is also applicable for determining the molecular formulae of complexes, spectrophotometrically, that one produced as products of incomplete equilibrium reactions.

In practice an equilibrium solutions of the two reactants are mixed in varying ratios and the absorbance of each mixture is determined at a selective wavelength. The absorbance is plotted against the mole fraction of the metal or ligand in the flasks. The resulting curves are called as jobs plots. The ratios that corresponds to the mole fractions the components in the complex will attain a maximum absorbance value. The positions of the maximum indicates the ligand : metal ratio of the complex in solution. For eg. a maximum corresponding

to 0.5 on the mole fraction ratio of the ligand scale shows a complex of 1:1 composition, while maximum at 0.67 and 0.75 indicates complexes of 2:1 & 3:1 ligand : Metal ratios respectively. The value of maxima is the value of ‘n’ in the formula of the complex, thus one can determine the formula of the complex.

Experimental

In this project work we have used this method of variation to study the ratio of metal ion and ligand in certain complexes in this project work.

In experimental study the five different complexes were performed

1) **Copper –EDTA Complex**
2) **Cobalt –Hydrazinate complex**
3) **Nickel – Hydrazinate complex**
4) **Zinc – EDTA Complex**
5) **Chloro Cuprate complex**
6) **Chloro Nickelate Complex**

Absorbance for each of the above complexes were measured by Systronics UV- Visible Spectrophotometer.

1) Copper(II) – EDTA Complex

Procedure: 0.005M solution of $CuSO_4.5H_2O$ by dissolving 0.4653 gms in 250ml of distilled water. Similary 0.005M solution of EDTA was prepared. Instrument was standardised using water as reference to measure absorbance as zero at the wavelength of 740 nm. In a beaker 3 ml of $CuSO_4$ and 27 ml of EDTA solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 740nm. Similarly absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $CuSO_4$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum absorbance value from the graph and the corresponding volume of reactant, value of 'n' is calculated while metal ligand ratio in the complex.

$$\mathbf{XL = V_L / V_L + V_M^o}$$

Where V_L - is the volume of the titrant added at each

V_M^o - is the initial volume of metal titrant.

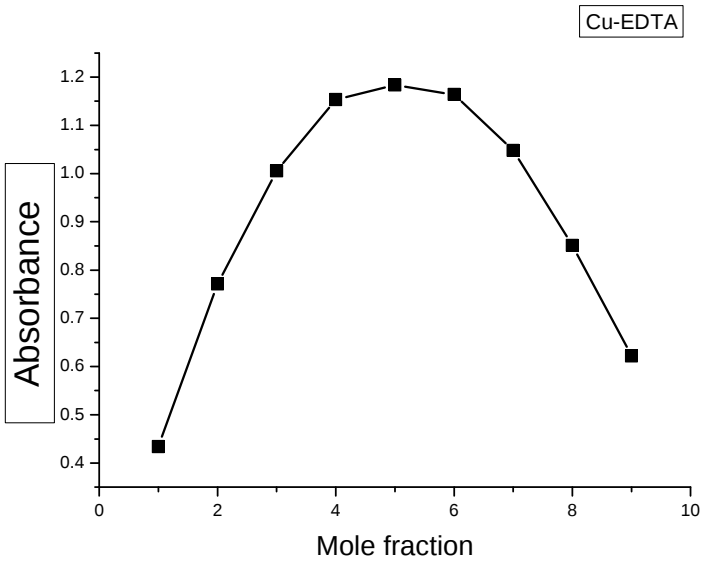
15/30 = 0.5

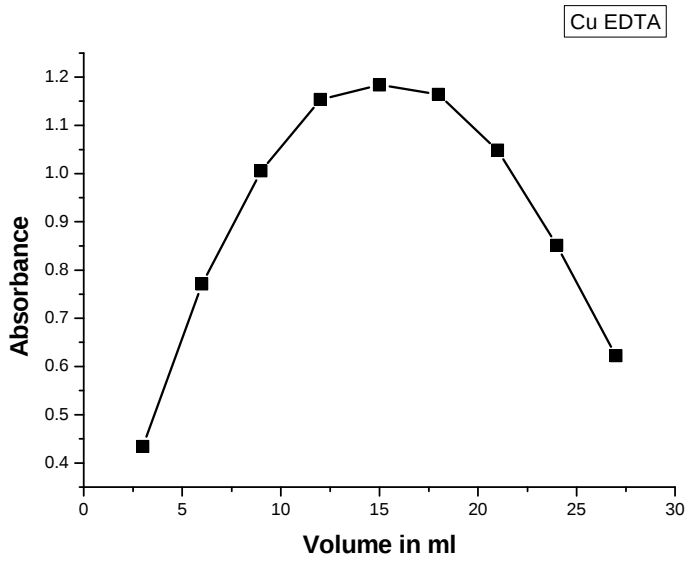
The value of n = 0.5 indicates that in the $CuSO_4.5H_2O$ & EDTA complex the metal to ligand ratio is 1:1.

The graph 1a & 1b shows the photometric curve at 740 nm by titrating solution A with solution B, the graphs are given below.

Observation Table

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactants
3	27	0.4339	0.9
6	24	0.7713	0.8
9	21	1.0051	0.7
12	18	1.1532	0.6
15	15	1.1836	0.5
18	12	1.1639	0.4
21	9	1.0481	0.3
24	6	0.8512	0.2
27	3	0.6219	0.1





Conclusion: Since the plot exhibit at XCu^{2+}= 0.5, it indicates the formulation of 1:1 complex.

2. Cobalt – Hydrazido complex:

Procedure: 0.005M solution of $CoCl_2.6H_2O$ by dissolving 0.2967 gms in 250ml of distilled water. Similarly 0.005M solution of $NH_2.NH_2.H_2O$ was prepared. Instrument was standardised using water as reference to measure absorbance as zero at the wavelength of 635 nm. In a beaker 3 ml of $CoCl_2.6H_2O$ and 27 ml of $NH_2.NH_2.H_2O$ solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 635nm. Similarly absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $CoCl_2.6H_2O$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum absorbance value from the graph and the corresponding volume of reactant, value of 'n' is calculated while metal ligand ratio in the complex.

Observation Table

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactants

3	27	0.2199	0.9
6	24	0.4062	0.8
9	21	0.4662	0.7
12	18	0.5022	0.6
15	15	0.5486	0.5
18	12	0.4987	0.4
21	9	0.4540	0.3
24	6	0.4132	0.2
27	3	0.3581	0.1

Calculations:

$$\mathbf{XL = V_L / V_L + V_M^o}$$

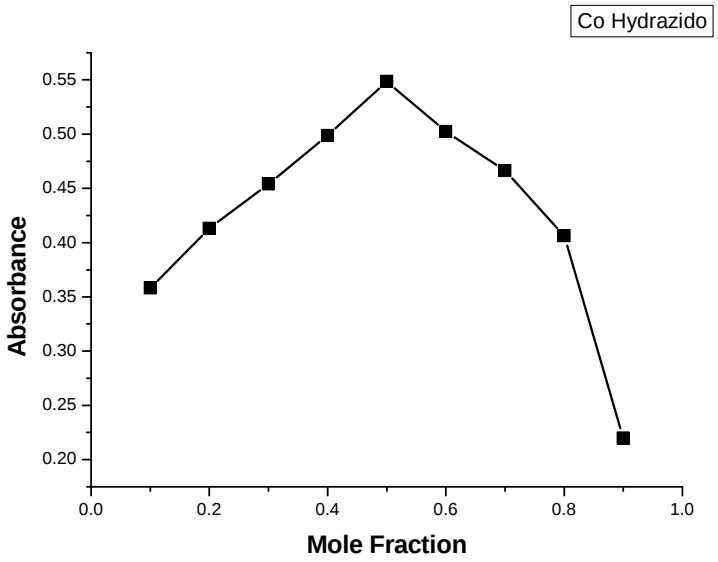
Where V_L - is the volume of the titrant added at each

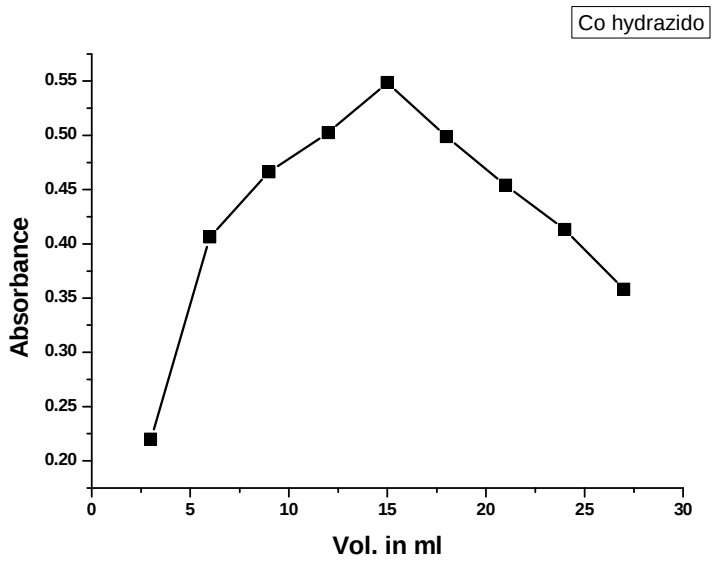
V_M^o - is the initial volume of metal titrant.

15/30 = 0.5

The value of n = 0.5 indicates that in the $CoCl_2.6H_2O$ & NH_2. $NH_2.H_2O$ complex the metal to ligand ratio is 1:1.

The graph 2a & 2b shows the photometric curve at 635nm by titrating solution A with solution B, the graphs are given below.





Conclusion: Since the plot exhibit at X Co^{2+}= 0.5, it indicates the formulation of 1:1 complex.

3. Nickel – Hydrazinate complex

Procedure: 0.005M solution of $Ni(NO_3)_2.6H_2O$ by dissolving 0.2967 gms in 250ml of distilled water. Similarly 0.005M solution of $NH_2.NH_2.H_2O$ was prepared. Instrument was standardised using water as reference to measure absorbance as zero at the wavelength of 285 nm. In a beaker 3 ml of $Ni(NO_3)_2.6H_2O$ and 27 ml of $NH_2.NH_2.H_2O$ solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 285 nm. Similarly absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $Ni(NO_3)_2.6H_2O$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum absorbance value from the graph and the corresponding volume of reactant, value of 'n' is calculated while metal ligand ratio in the complex.

Observation Table

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactants
3	27	0.3160	0.9
6	24	0.3342	0.8
9	21	0.3886	0.7
12	18	0.4543	0.6
15	15	0.5447	0.5

18	12	0.4481	0.4
21	9	0.4220	0.3
24	6	0.3846	0.2
27	3	0.3222	0.1

Calculations:

$$\mathbf{XL = V_L / V_L + V_M^o}$$

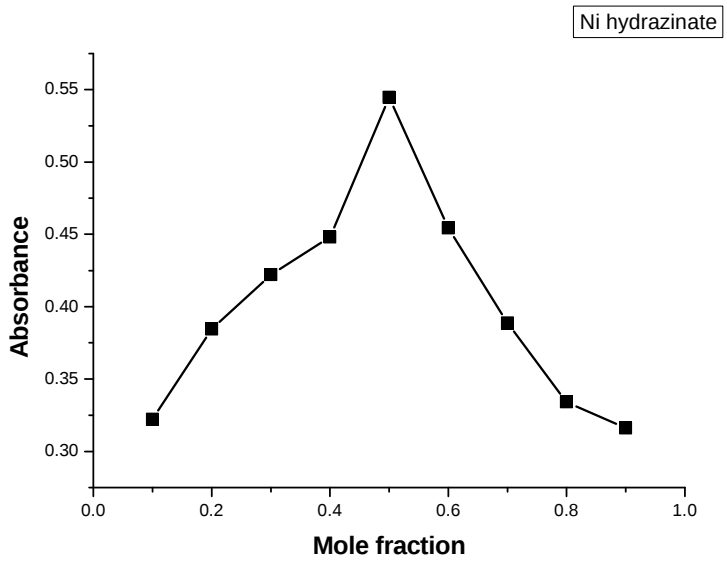
Where V_L - is the volume of the titrant added at each

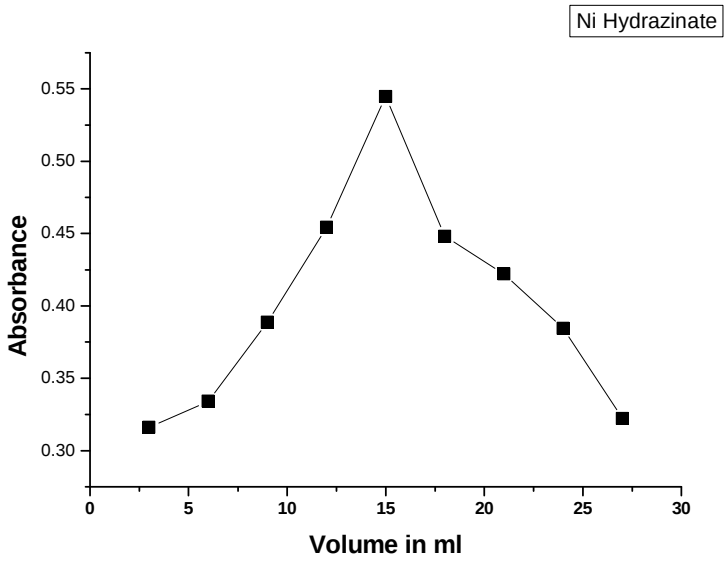
V_M^o - is the initial volume of metal titrant.

15/30 = 0.5

The value of n = 0.5 indicates that in the $Ni(NO_3)_2.6H_2O$ & $NH_2.NH_2.H_2O$ complex the metal to ligand ratio is 1:1.

The graph 3a & 3b shows the photometric curve at 635nm by titrating solution A with solution B, the graphs are given below.





Conclusion: Since the plot exhibit at X Ni^{2+}= 0.5, it indicates the formulation of 1:1 complex.

4. Zn – EDTA Complex

Procedure: 0.005M solution of $ZnSO_4$.$7H_2O$ by dissolving 0.3344 gms in 250ml of distilled water. Similarly 0.005M solution of EDTA was prepared. Instrument was standardised using water as reference to measure absorbance as zero at the wavelength of 240 nm. In a beaker 3 ml of $ZnSO_4$ and 27 ml of EDTA solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 740nm. Similarly absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $ZnSO_4$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum absorbance value from the

graph and the corresponding volume of reactant, value of ‘n’ is calculated while metal ligand ratio in the complex.

$$\mathbf{XL = V_L / V_L + V_M^{\circ}}$$

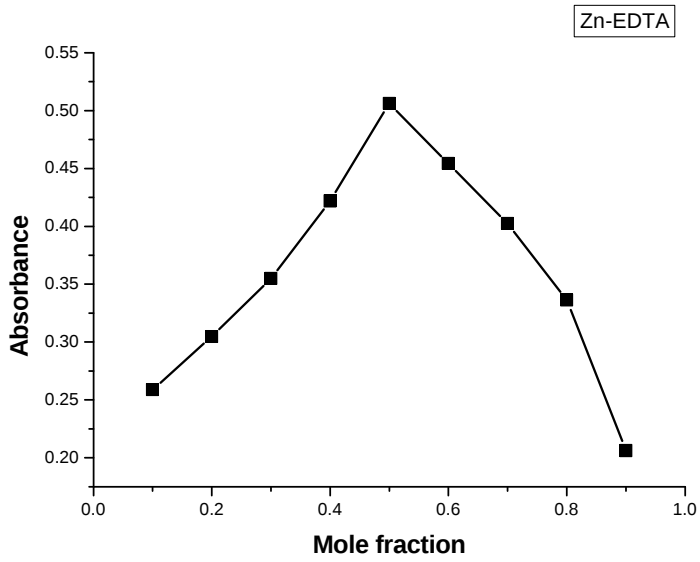
Where V_L - is the volume of the titrant added at each

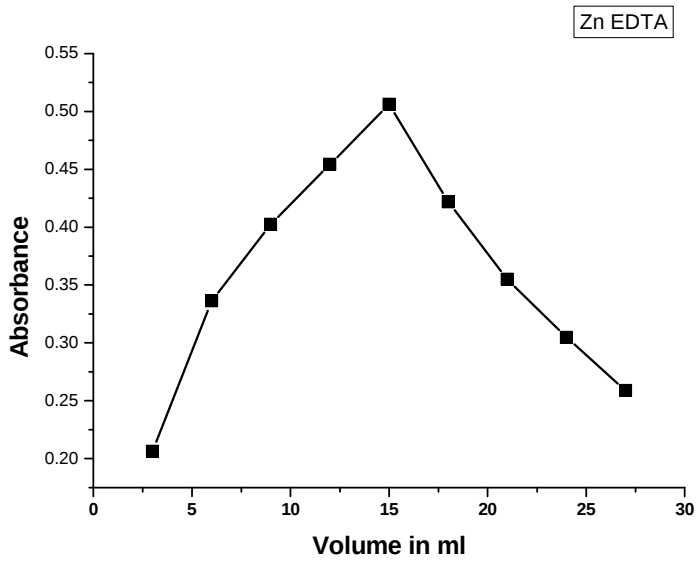
V_M° - is the initial volume of metal titrant.

15/30 = 0.5

Observation Table

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactants
3	27	0.2061	0.9
6	24	0.3362	0.8
9	21	0.4024	0.7
12	18	0.4543	0.6
15	15	0.5061	0.5
18	12	0.4220	0.4
21	9	0.3549	0.3
24	6	0.3047	0.2
27	3	0.2589	0.1





Conclusion: Since the plot exhibit at XZn^{2+}= 0.5, it indicates the formulation of 1:1 complex.

5. Chloro Cuprate complex:

Procedure: 0.005M solution of $CuSO_4$.$5H_2O$ by dissolving 0.4653 gms in 250ml of distilled water. Similary 0.005M solution of KCl was prepared. Instrument was standardised using water as reference to measure absorbance as zero at the wavelength of 275 nm. In a beaker 3 ml of $CuSO_4$ and 27 ml of KCl solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 275 nm. Similarly absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $CuSO_4$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum absorbance value from the graph and the corresponding volume of reactant, value of 'n' is calculated while metal ligand ratio in the complex.

$$\mathbf{XL = V_L / V_L + V_M^o}$$

Where V_L - is the volume of the titrant added at each

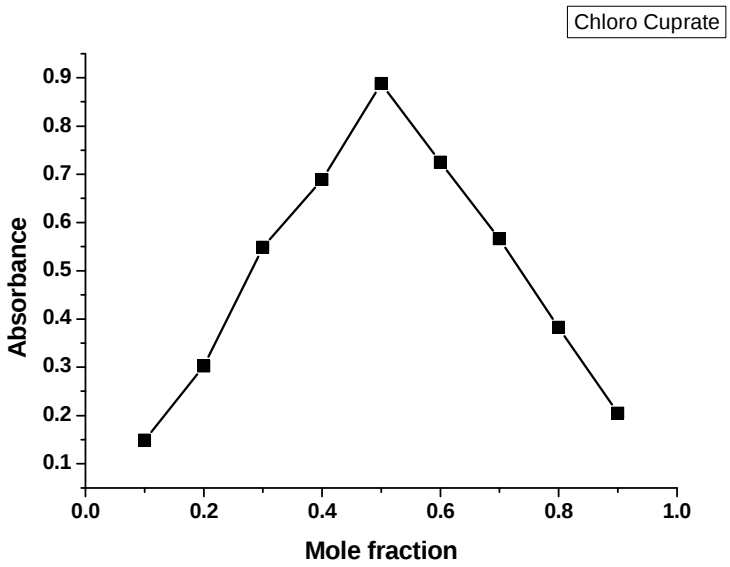
V_M^o - is the initial volume of metal titrant.

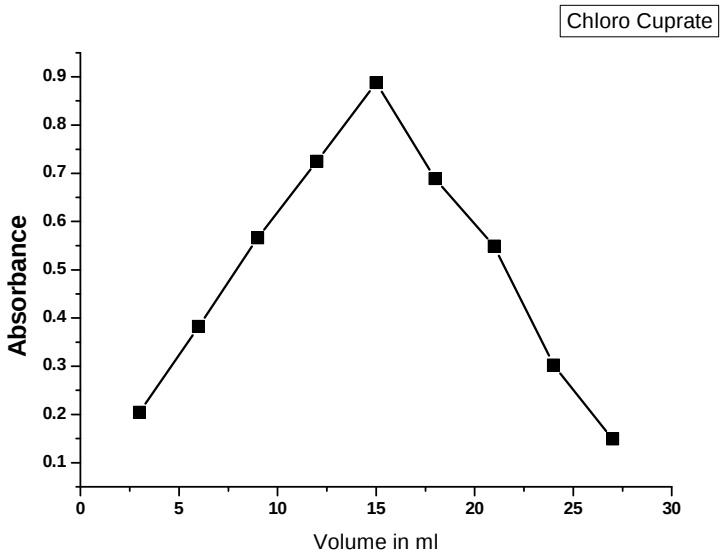
15/30 = 0.5

Observation Table

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactants
3	27	0.2046	0.9

6	24	0.3826	0.8
9	21	0.5663	0.7
12	18	0.7248	0.6
15	15	0.8880	0.5
18	12	0.6885	0.4
21	9	0.5486	0.3
24	6	0.3024	0.2
27	3	0.1488	0.1





Conclusion: Since the plot exhibit at XCu^{2+}= 0.5, it indicates the formulation of 1:1 complex.

6. **Chloro Nickelate complex**

Procedure: 0.005M solution of $Ni(NO_3)_2.6H_2O$ by dissolving 0.3121 gms in 250ml of distilled water. Similarly 0.005M solution of KCl was prepared. Instrument was standardised using water as reference to measure absorbance as zero at the wavelength of 310 nm. In a beaker 3 ml of $Ni(NO_3)_2.6H_2O$ and 27 ml of KCl solution and was used as sample no. 1. The solution was taken in cuvette and absorbance was measured at 310 nm. Similarly absorbance's for nine different concentration ratios varying from 3:27 to 27:3 w.r.t $Ni(NO_3)_2.6H_2O$ solution at the same wavelength. The absorbance obtained was plotted vs volume of either solution used in the complex formation. The plot shows a parabolic graph and using the maximum

absorbance value from the graph and the corresponding volume of reactant, value of ‘n’ is calculated while metal ligand ratio in the complex.

$$\mathbf{XL = V_L / V_L + V_M^{\circ}}$$

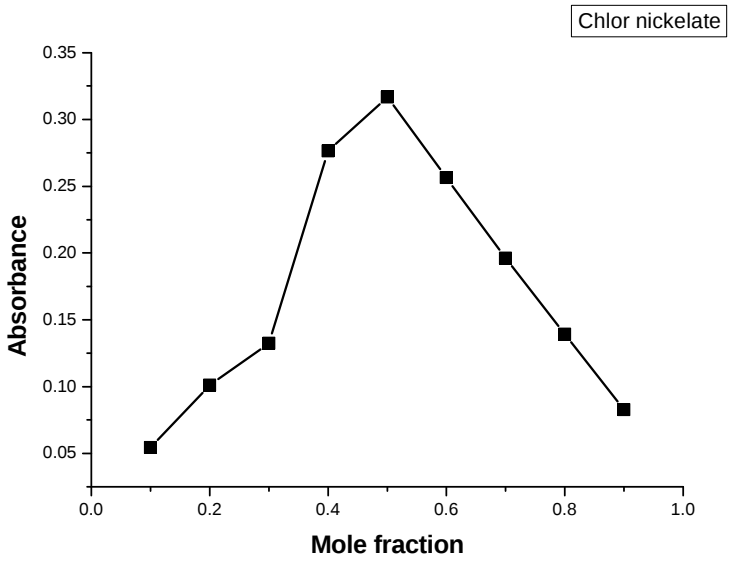
Where V_L - is the volume of the titrant added at each

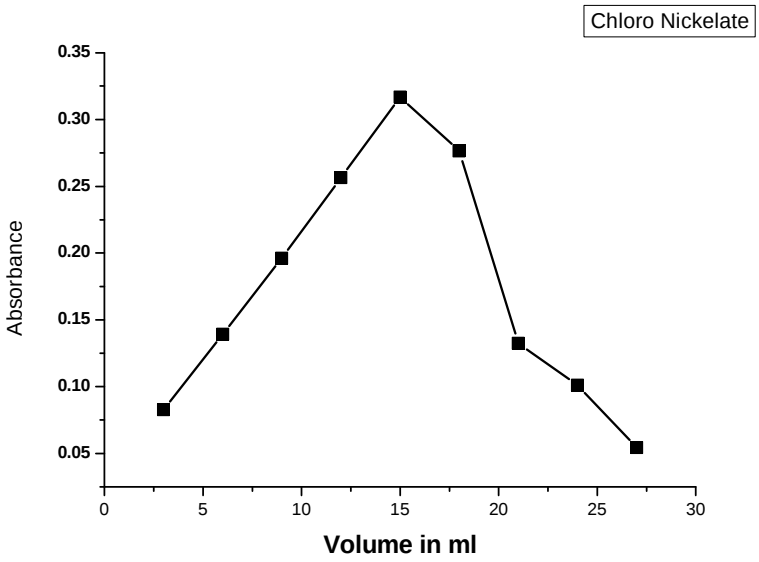
V_M° - is the initial volume of metal titrant.

15/30 = 0.5

Observation Table

Solution A In ml	Solution B In ml	Absorbance value	Mole fraction of the reactants
3	27	0.0827	0.9
6	24	0.1392	0.8
9	21	0.1962	0.7
12	18	0.2564	0.6
15	15	0.3169	0.5
18	12	0.2764	0.4
21	9	0.1323	0.3
24	6	0.1012	0.2
27	3	0.0543	0.1





Conclusion: Since the plot exhibit at XNi^{2+}= 0.5, it indicates the formulation of 1:1 complex.