

CHROMONE 6-BENZOYLHYDRAZONE COMPLEXES OF SOME TRANSITION METALS

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Abstract. Metal complexes of 2-methyl 5-methoxy 7-hydroxy chromone 6-benzoylhydrazone with some divalent transition metal ions were investigated by the use of spectrophotometric, electric conductance, pH titration and ir measurements. Isolation of solid complexes and physical measurements revealed the existence of mono- and *bis*-ligand complexes. Complex formation is shown to take place through a proton displacement from the hydroxyl group in the 7-position of the chromone residue of the ligand. The azomethine and carbonyl groups of chromone and benzoyl hydrazide residues are also involved in coordination.

During recent years there has been an increased interest in Schiff's base complexes of transition metals. The interest in such studies arose mainly from structural problems.¹⁻⁴ It was found that chelation through the azomethine group is stabilized by the presence of auxochrome group in the *ortho*-position. It was also found that the presence of a hydroxyl group in an opposition to the hydrazone bearing carbon atom is not enough for complex formation but this hydroxyl group must also possess considerable acidic properties.¹⁻⁴

Also, studies on the metal chelates of acid hydrazides revealed that two types of interactions (keto and enol forms) are liable to take place.⁵⁻⁷

The present work deals with complexes formed by the interaction of 2-methoxy 7-hydroxy chromone 6-benzoylhydrazone with Cu (II), Co (II), Ni (II), Mn (II), Zn (II) and Cd (II) in alcoholic solution. It is necessary not to rely in general on any one of the many methods known for determining the existence and structure of complex compounds. For this reason isolation of pure compounds spectrophotometric, electrical conductance, pH titration and ir measurements were carried out to elucidate the nature of the complexes under consideration. Also, the use of this ligand as a microanalytical reagent for the spectrophotometric determination of metals in solution was also considered.

Materials and Methods

Analar or Merck grade metal salts were used for preparing molar solutions. The weighed amounts of salts or ligand were dissolved in the requisite volumes of absolute ethanol. Determinations of chloride and metal contents were performed by standard known procedures. Microanalysis of C, H and N was undertaken by the microanalytical unit

of the University of Cairo. The results of analysis are given in Table 1.

Preparation of Compounds. The ligand was obtained by the condensation of benzoyl-hydrzaine⁸ with 2-methyl 5-methoxy 6-formyl 7-hydroxy chromone, as prepared by the oxidation of visnagine with potassium dichromate.⁹ The product was recrystallized from ethanol, m.p. > 280°.

The solid complexes were prepared by mixing 0.3 g. the ligand with a suitable weight of metal salt followed by the addition of 20 ml. absolute ethanol. The mixture was then refluxed on a water bath for about 2 hr. Mono-ligand complexes were obtained by mixing equimolecular amounts of the ligand and the metal salt whereas *bis*-ligand complexes separated out when excess ligand was added. No more than *bis*-ligand complex was obtained even in the presence of excess amounts of ligands. At the beginning, the materials dissolve forming a homogeneous solution; then the solid complexes start to precipitate. The yield increased as the reflux was continued. To ensure the isolation of pure complexes, the reaction product was filtered immediately while the solution was still hot. The solid complexes were washed several times with hot ethanol. All solid complexes isolated were insoluble in the majority of organic solvents and had melting points above 280°.

Working Procedures. Infrared spectra of solid complexes and the ligands were investigated by the KBr disc technique, using a Pye Unicam SP 1000 infrared spectrophotometer.

In spectrophotometric measurements volumes of 0.1 M methanolic solution of the metal chloride were added to the necessary volumes of 0.01 M ethanolic solution of the ligand, then diluted to 10 ml with absolute ethanol and thoroughly mixed. The absorp-

tion spectra of the resulting solutions were then recorded using a blank containing the same concentration of the ligand in ethanol.

In conductometric titration a known volume of the metal ion solution was placed in a 25-ml closed beaker of the tall type. This solution was then titrated with the ligand solution delivered from a micro-burette. The conductance values were measured using a Beckmann conductivity bridge. Volume correction was taken in consideration.

In pH titration 25 ml of 2×10^{-4} M solution in both ligand and the metal halide were titrated with 0.01 N NaOH solution. The pH values were measured using a Pye Unicam Model 290 pH meter.

Results and Discussion

Isolation of Pure Compounds. The interaction of 2-methyl 5-methoxy 7-hydroxy chromone 6-benzoylhydrazone (Ch. BH.) with the studied hydrated metal salts gave mono- and bis-ligand complexes. These were found to be insoluble in water and organic solvents such as acetone, alcohol, chloroform and carbon tetrachloride. Results of elemental analysis of the isolated complexes are given in Table 1.

Spectrophotometric Studies. Ethanolic solutions containing different proportions of Ch. BH. with Cu^{2+} , Co^{2+} and Ni^{2+} ions indicated characteristic absorption maxima at 300, 382; 298, 385 and 300, 392 nm respectively. This shows the formation of complexes in the three systems. Absorption spectra are represented in Fig. 1 (a, b, c).

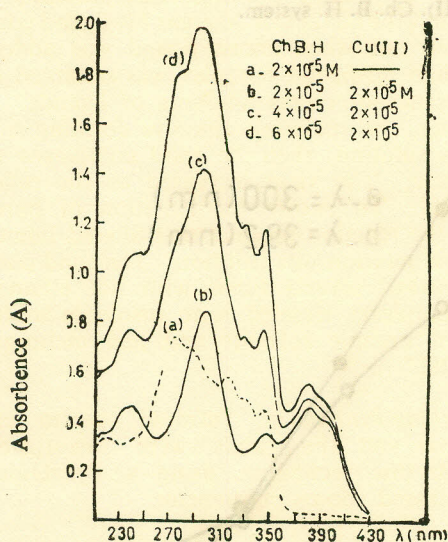


Fig. 1 (a). Absorption spectra of Cu (II). Ch. B. H. mixtures.

On keeping the metal ion concentration constant while changing that of the ligand, the optical density increases steadily and finally attains a more or less

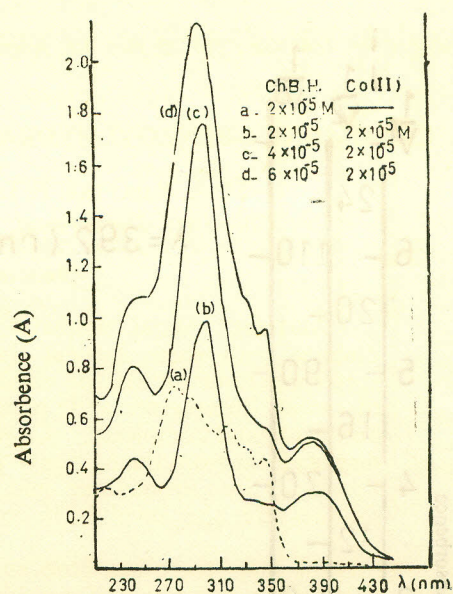


Fig. 1 (b). Absorption of Co (II)—Ch. B. H. mixtures.

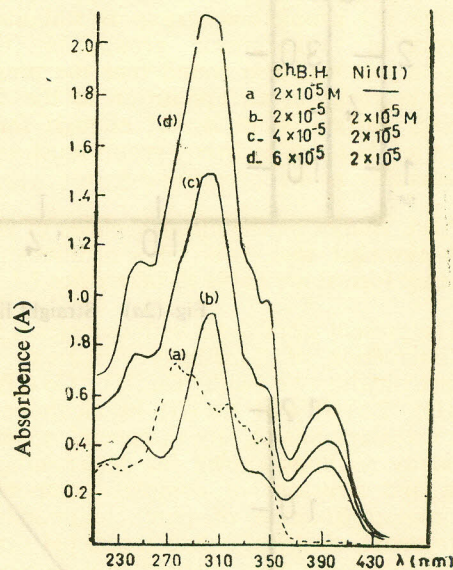


Fig. 1 (c). Absorption spectrum of Ni. Ch. B. H. mixtures.

constant value. When the solution contains a constant concentration of the ligand and variable quantities of the metal ions, the optical density increases regularly with the metal ion concentration. The plot of absorbance as a function of the metal ion concentration gave a straight line in the concentration range up to 3.5×10^{-5} M. Also the high ϵ values (2×10^4 , 1.5×10^4 , and 2.14×10^4 for Cu^{2+} , Co^{2+} and Ni^{2+} respectively) suggest the possible application of the method for the determination of small amounts of the pure metal ion.

The metal-ligand ratio of the complexes formed in solution was traced by applying the well known molar ratio,¹⁰ straight line,¹¹ continuous variation,¹²

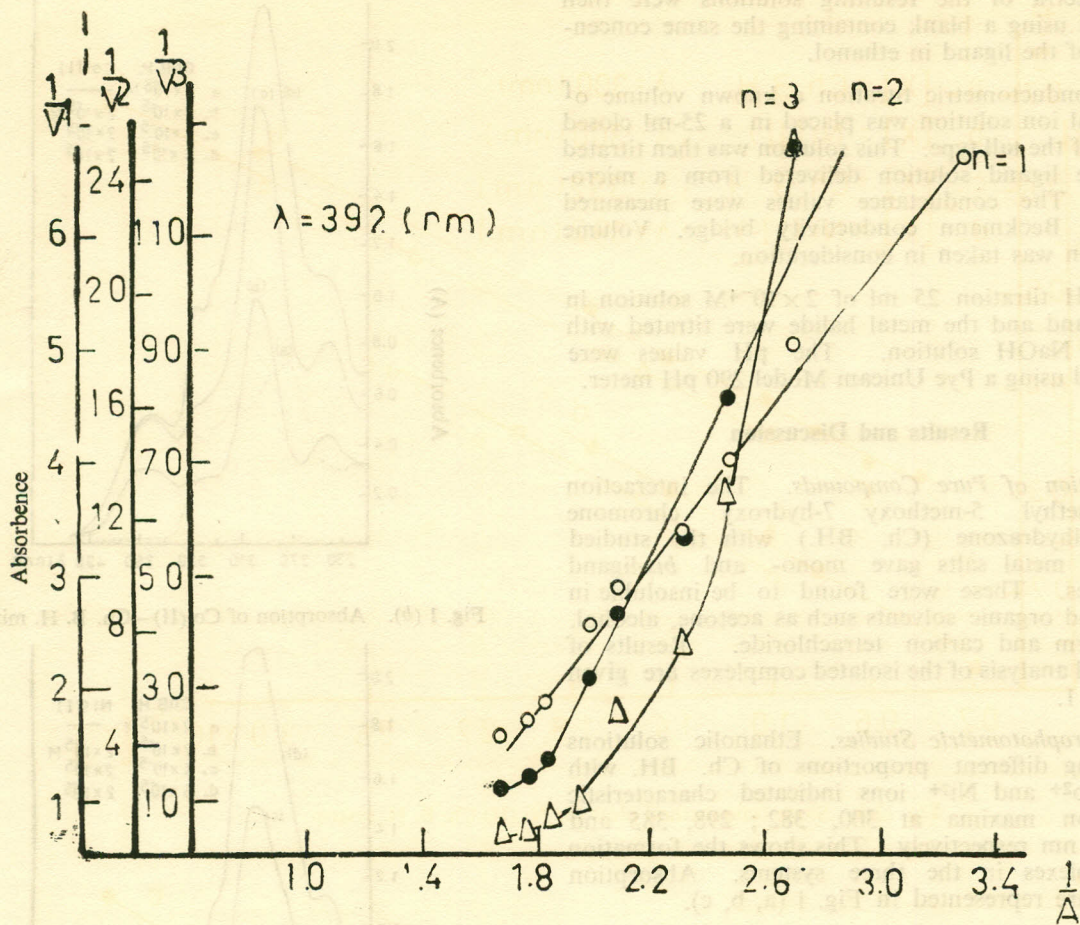


Fig. (2a). Straight line method plot of Ni (II). Ch. B. H. system.

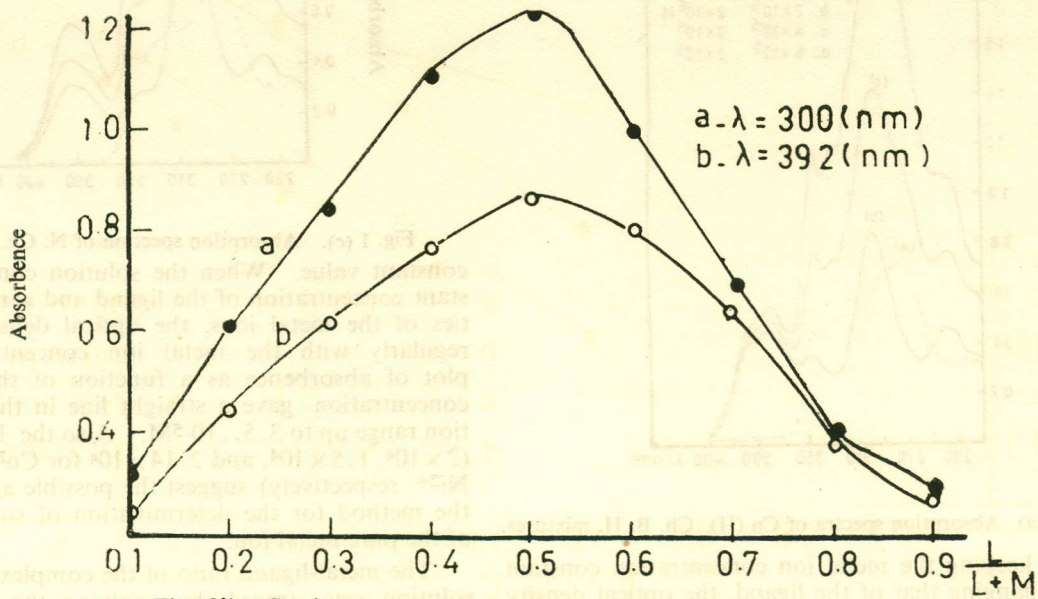


Fig. (2b). Continuous variation method plot for Ni (II). Ch. B. H. system.

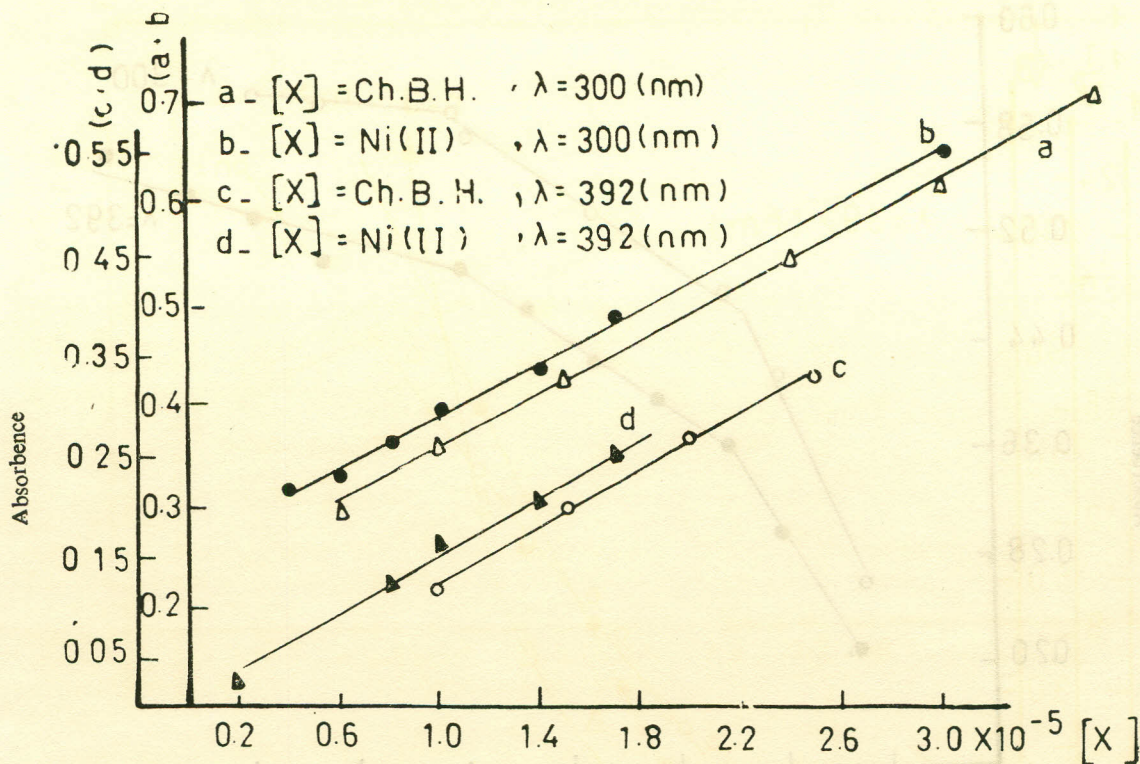


Fig. (2c). Slope ratio method plots for Ni (II) Ch. B. H. system.

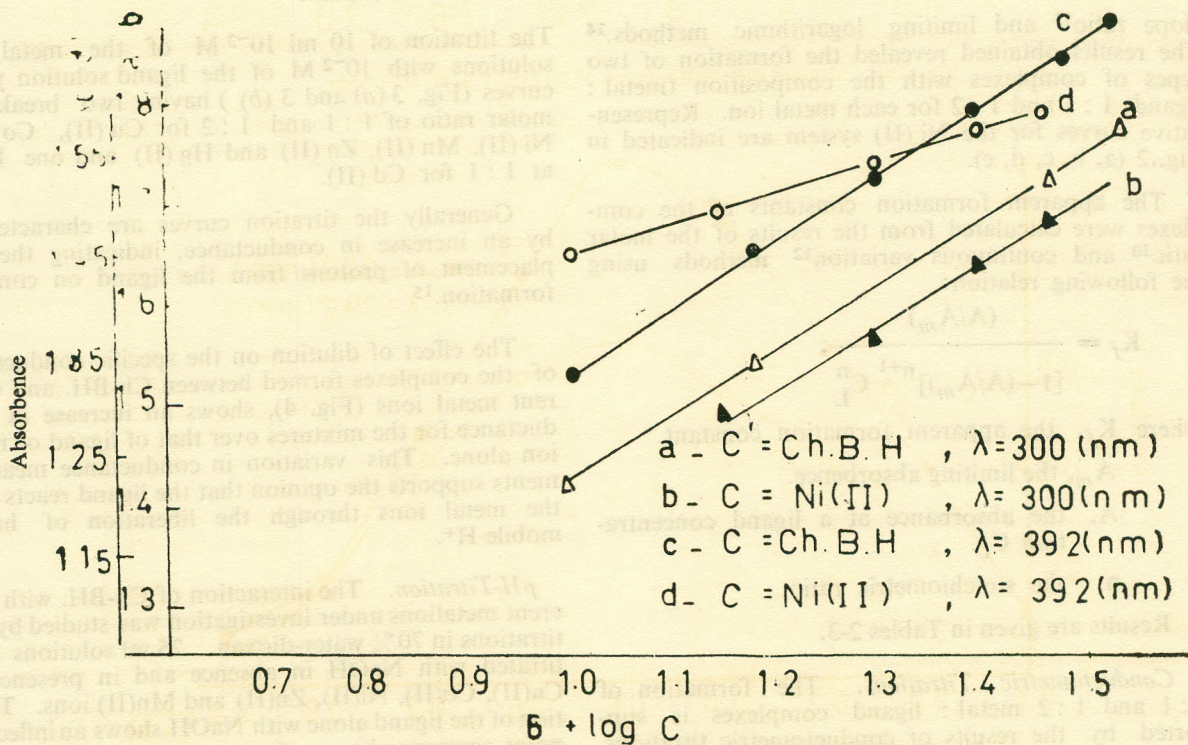


Fig. (2d). Limiting logarithmic method plots for Ni (II) Ch. B. H. system.

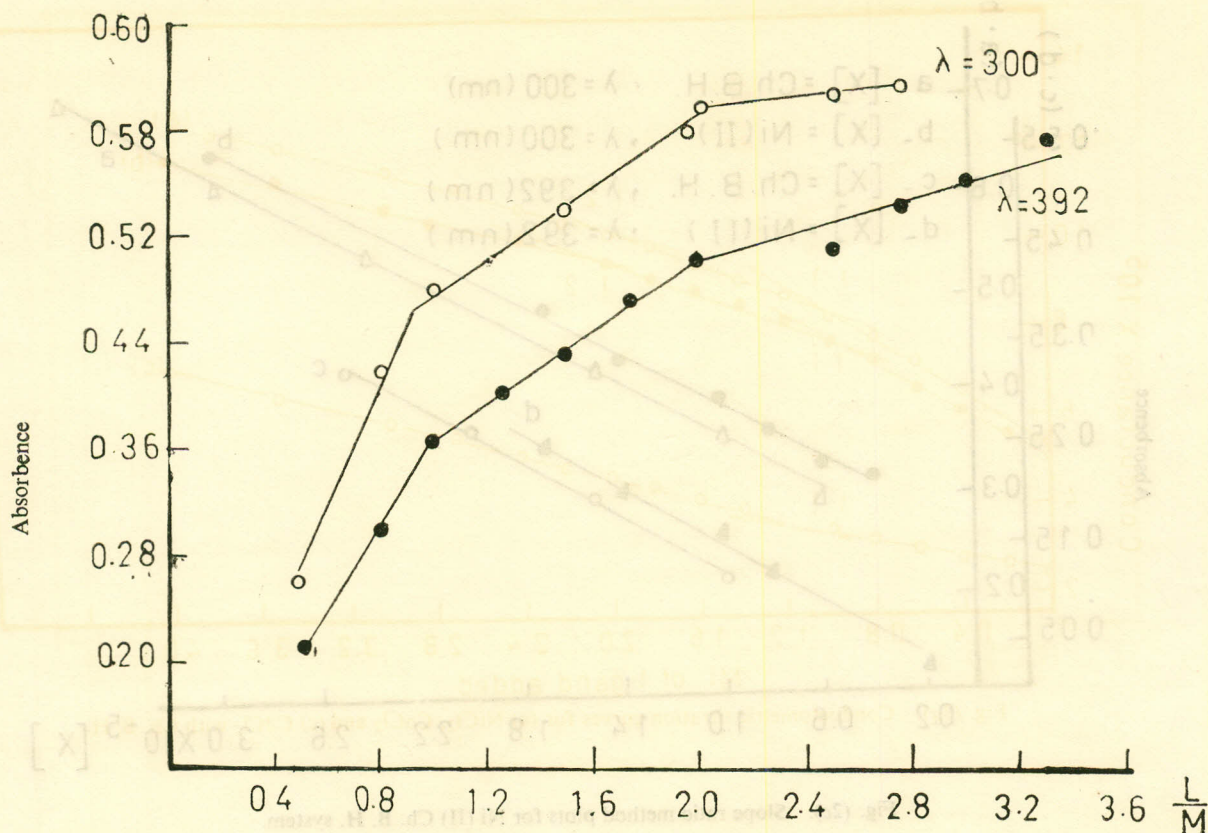


Fig. 3. Molar ratio plots for Ch. B. H. Ni (II) system.

slope ratio¹³ and limiting logarithmic methods.¹⁴ The results obtained revealed the formation of two types of complexes with the composition (metal : ligand) 1 : 1 and 1 : 2 for each metal ion. Representative curves for the Ni (II) system are indicated in Fig. 2 (a, b, c, d, e).

The apparent formation constants of the complexes were calculated from the results of the molar ratio¹⁰ and continuous variation¹² methods using the following relation:

$$K_f = \frac{(A/A_m)}{[1-(A/A_m)]^{n+1} C_L^n}$$

where K_f , the apparent formation constant.

A_m , the limiting absorbance.

A , the absorbance at a ligand concentration C_L .

n , the stoichiometric ratio.

Results are given in Tables 2-3.

Conductometric Titrations. The formation of 1 : 1 and 1 : 2 metal : ligand complexes is supported by the results of conductometric titrations.

The titration of 10 ml 10^{-3} M of the metal ion solutions with 10^{-2} M of the ligand solution yields curves (Fig. 3 (a) and 3 (b)) having two breaks at molar ratio of 1 : 1 and 1 : 2 for Cu (II), Co (II), Ni (II), Mn (II), Zn (II) and Hg (II) and one break at 1 : 1 for Cd (II).

Generally the titration curves are characterized by an increase in conductance, indicating the displacement of protons from the ligand on complex formation.¹⁵

The effect of dilution on the specific conductance of the complexes formed between Ch-BH. and different metal ions (Fig. 4), shows an increase in conductance for the mixtures over that of ligand or metal ion alone. This variation in conductance measurements supports the opinion that the ligand reacts with the metal ions through the liberation of highly mobile H^+ .

pH-Titration. The interaction of Ch-BH. with different metal ions under investigation was studied by pH titrations in 70% water-dioxan. 25 ml solutions were titrated with NaOH in absence and in presence of Cu(II), Co(II), Ni(II), Zn(II) and Mn(II) ions. Titration of the ligand alone with NaOH shows an inflection point corresponding to the consumption of two equi-

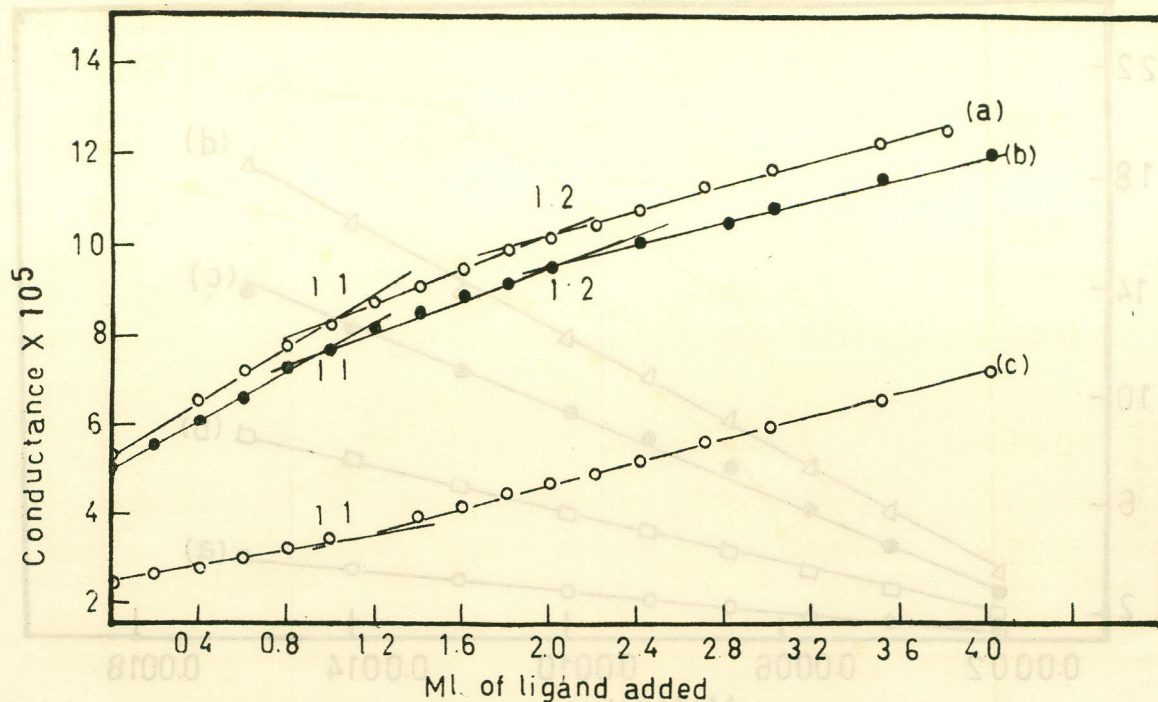


Fig. (3a). Conductometric titration curves for (a) NiCl₂, CoCl₂ and (c) CdCl₂ with Ch. B. H.

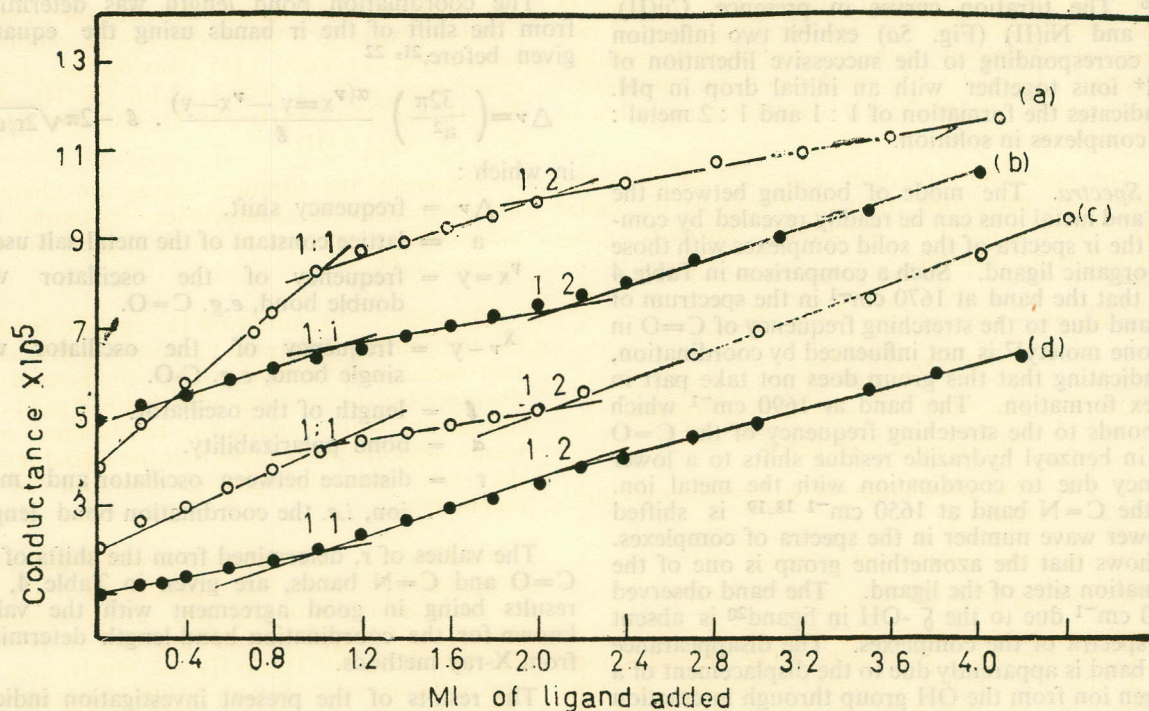


Fig. (3b). Conductometric titration curves for (a) CuCl₂, (b) MnCl₂, (c) ZnCl₂ and (d) HgCl₂ with Ch. B. H.

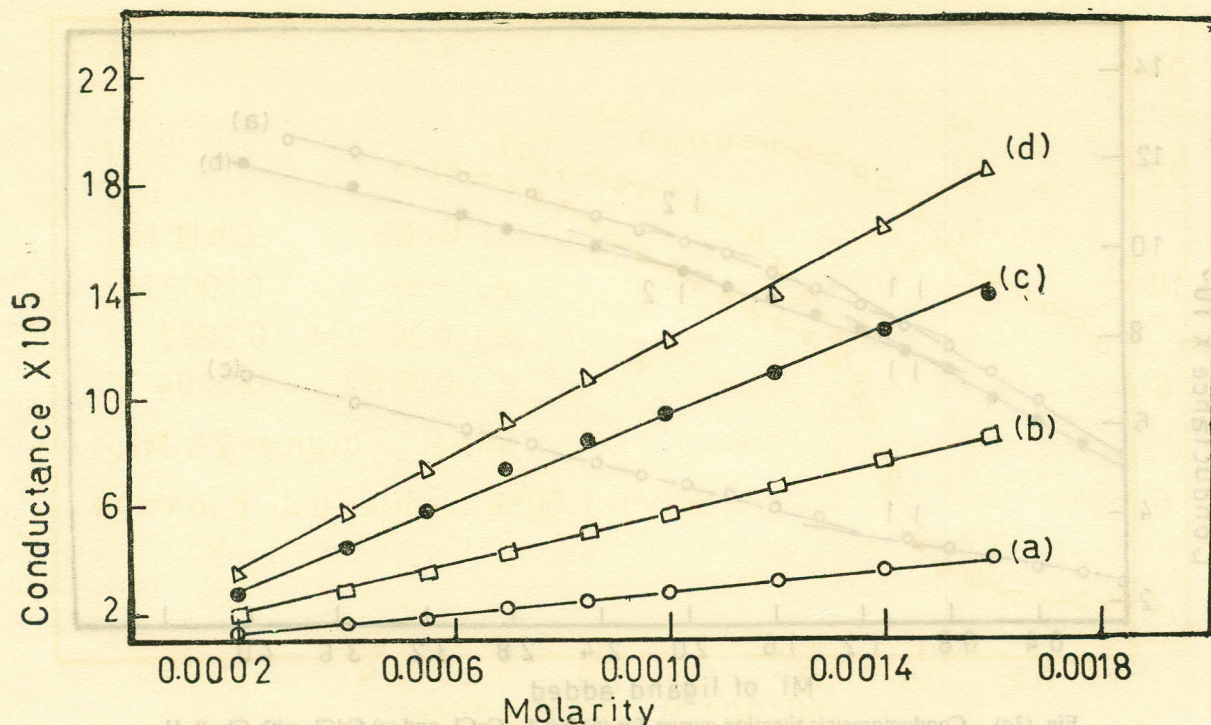


Fig. 4. Increase of conductance on interaction between CoCl_2 and Ch. B. H. (a) Ch. B. H. (b) CoCl_2 , (c) $\text{CoCl}_2 + \text{Ch. B. H. (1:1)}$ and (d) $\text{CoCl}_2 + \text{Ch. B. H. (1:2)}$.

valents of alkali due to the simultaneous liberation of two H^+ ions. The start of the curve at a pH value slightly higher than 7 was observed in similar cases.¹⁶ The titration curves in presence Cu(II) , Co(II) and Ni(II) (Fig. 5a) exhibit two inflection points corresponding to the successive liberation of two H^+ ions together with an initial drop in pH. This indicates the formation of 1:1 and 1:2 metal:ligand complexes in solution.

IR Spectra. The mode of bonding between the ligand and metal ions can be readily revealed by comparing the ir spectra of the solid complexes with those of the organic ligand. Such a comparison in Table 4 shows that the band at 1670 cm^{-1} in the spectrum of the ligand due to the stretching frequency of C=O in chromone moiety¹⁷ is not influenced by coordination, thus indicating that this group does not take part in complex formation. The band at 1690 cm^{-1} which corresponds to the stretching frequency of the C=O group in benzoyl hydrazide residue shifts to a lower frequency due to coordination with the metal ion. Also, the C=N band at 1650 cm^{-1} ^{18,19} is shifted to a lower wave number in the spectra of complexes. This shows that the azomethine group is one of the coordination sites of the ligand. The band observed at 1350 cm^{-1} due to the $\xi\text{-OH}$ in ligand²⁰ is absent in the spectra of the complexes. The disappearance of this band is apparently due to the displacement of a hydrogen ion from the OH group through interaction with the metal ions. The spectra also show a broad

absorption band in the 3400 cm^{-1} region characteristic of water molecules present in the chelates.

The coordination bond length was determined from the shift of the ir bands using the equation given before.^{21, 22}

$$\Delta\nu = \left(\frac{32\pi}{a^2} \right) \frac{\alpha(\nu_{x=y} - \nu_{x-y})}{\ell} \cdot \ell - 2\pi\sqrt{2r/a}$$

in which :

$\Delta\nu$ = frequency shift.

a = lattice constant of the metal salt used.

$\nu_{x=y}$ = frequency of the oscillator with double bond, e.g. C=O .

ν_{x-y} = frequency of the oscillator with single bond, e.g. C-O .

ℓ = length of the oscillator.

α = bond polarizability.

r = distance between oscillator and metal ion, i.e. the coordination bond length.

The values of r , determined from the shifts of the C=O and C=N bands, are given in Table 4, the results being in good agreement with the values known for the coordination bond length determined from X-ray methods.

The results of the present investigation indicate that the chelating agents under investigation behave

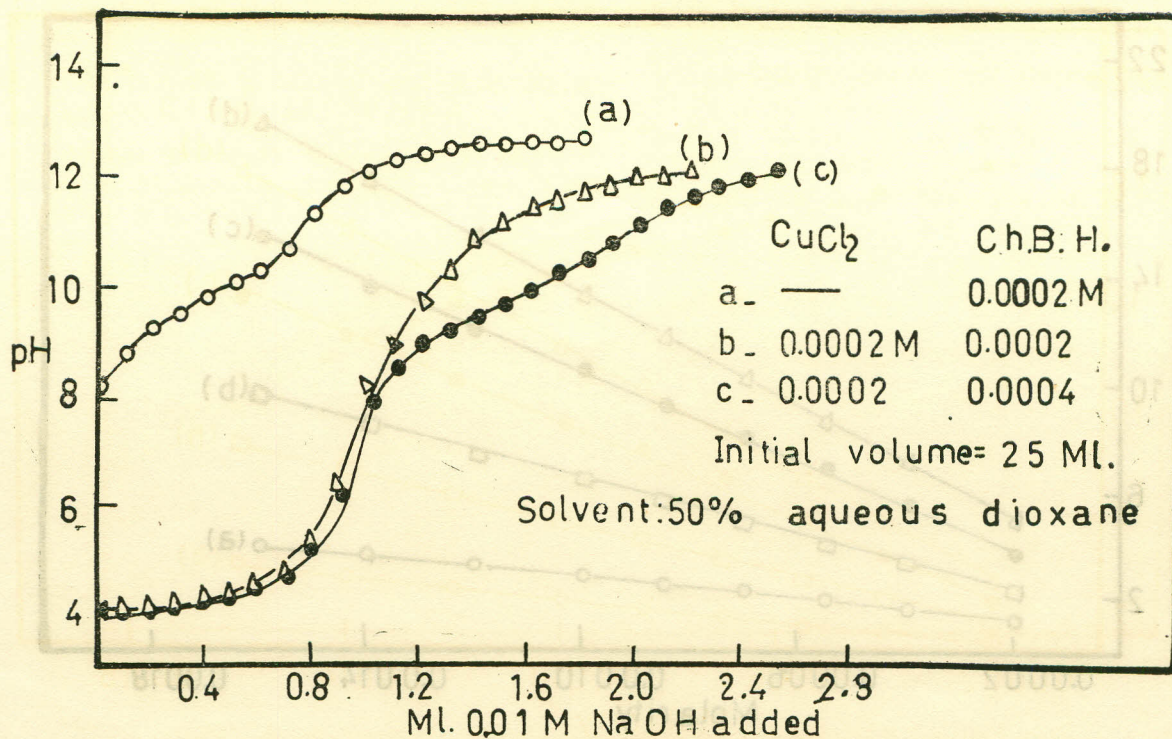


Fig. (5a). Titration curves of Ch. B. H. in absence and in presence of CuCl₂ with 0.01 M NaOH.

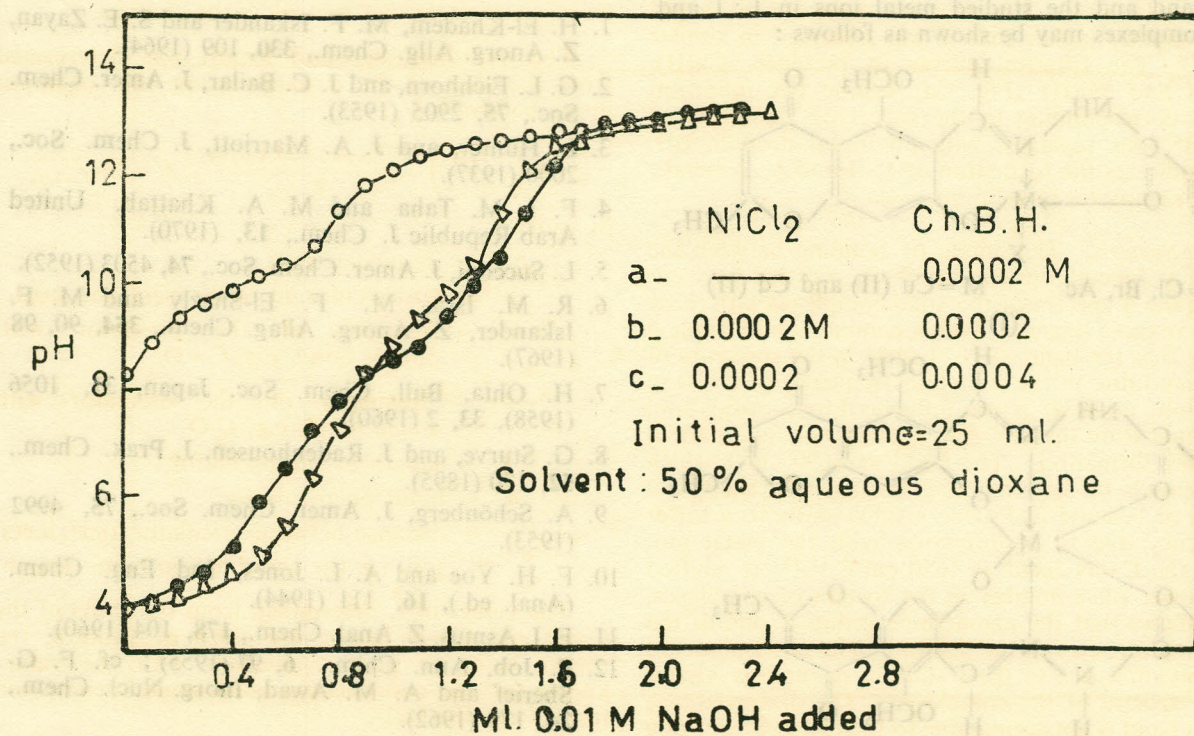


Fig. (5b). Titration curves of Ch. B. H. in absence and in presence of NiCl₂ with 0.01 M NaOH.

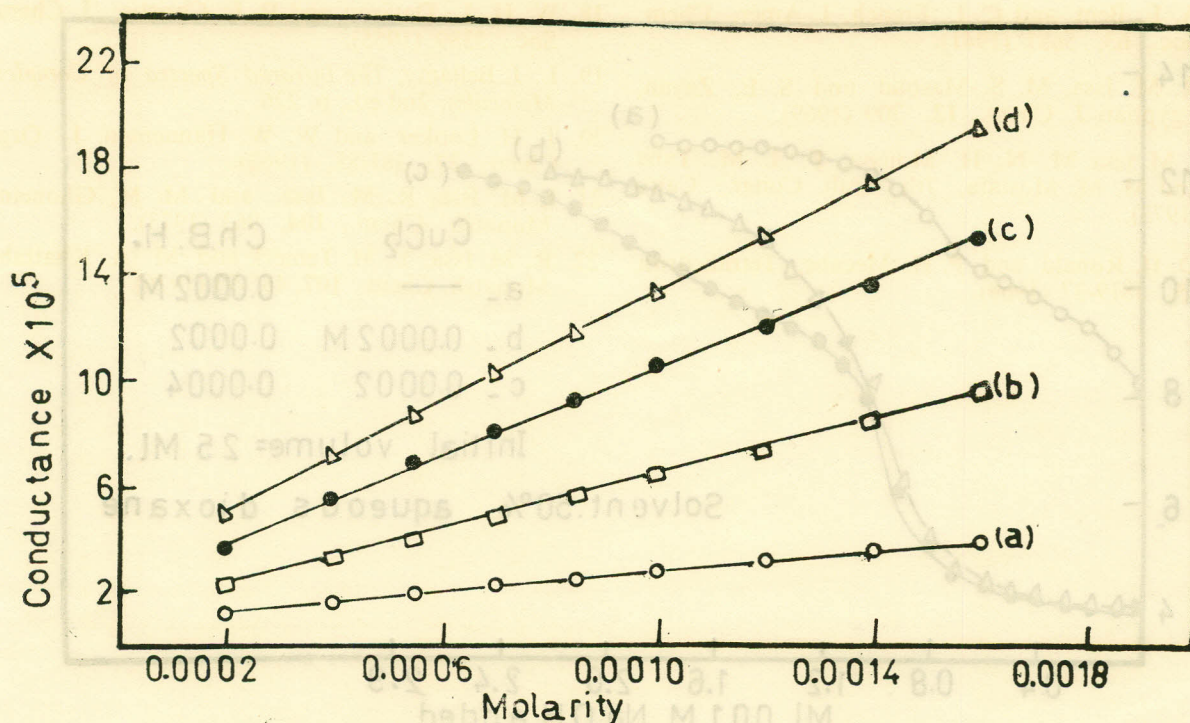
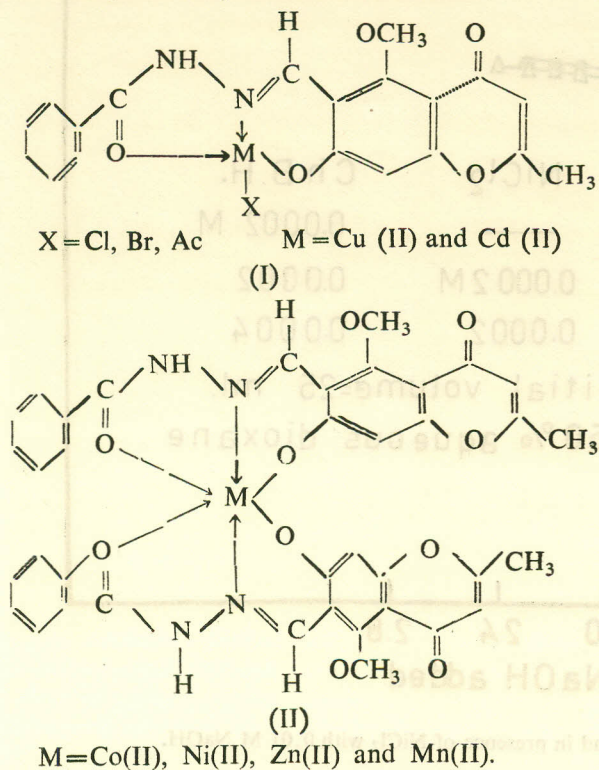


Fig. 6. Increase of conductance on interaction between NiCl_2 and Ch. B. H. (a) Ch. B. H. (b) NiCl_2 , (c) $\text{NiCl}_2 + \text{Ch. B. H. (1 : 1)}$ and (d) $\text{NiCl}_2 + \text{Ch. B. H. (1 : 2)}$.

as tridentate ligands. The mode of bonding between the ligand and the studied metal ions in 1 : 1 and 1 : 2 complexes may be shown as follows :



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Hydrochloric acid (1-4 N), perchloric acid (1-10%), acetic acid (5-20% to glacial) and sulphuric acid (1-12 N) were used to find out suitable media for quantitative oxidation of platinum (II) to platinum (IV) but 10N H₂SO₄ turned out to be the best.

TABLE DETERMINATION OF MICROGRAMME AMOUNTS OF PLATINUM WITH COBALT (III) ACETATE IN 10N H₂SO₄

No.	Amount taken (µg)	Amount found (µg)	Standard deviation (%)
1	25.34	25.43	0.03%
2	30.67	30.70	0.04%
3	121.20	121.49	0.13%
4	252.36	252.20	0.08%
5	324.70	324.44	0.08%
6	202.72	202.19	0.04%
7	760.01	712.07	0.03%

The oxidation of platinum (II) to platinum (IV) was quantitative in this medium and the potential jump at equivalence point was quite reasonable. With the increasing amount of platinum being taken, the potential jump showed an increasing trend but after a certain limit it started decreasing to the extent that with further increase in the platinum taken the oxidation did not proceed quantitatively, i.e. there did not appear any potential jump at the equivalence point. But for the amount as reported in the Table the oxidation was quantitative. The time taken to complete one titration went on increasing with the increasing amount of platinum but within the limits exhibited in the Table the reaction proceeded at a reasonable rate and results of analytical importance were available.

According to the method reported platinum can be determined within the limits from 25.34 µg to 760.01 µg with a maximum standard deviation of 0.13%.

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The high redox potential of cobalt (III) acetate has been successfully utilized by the authors for the determination of a variety of compounds.¹⁻⁵ These studies encouraged the authors to explore further possibilities of the volumetric oxidimetric use of this promising titan for the standardization of analytical methods for various other compounds.

Volumetric procedures for the determination of platinum metals remain a fertile field for analytical chemists. In view of the state of affairs we have in a previous communication reported the results of ruthenium determination via its oxidation with the titan.⁶ In order to extend its scope as a volumetric reagent for the determination of platinum metals we have tried to evolve a method for platinum (IV) estimation and the results of this study are reported here.

Experimental

Reagents: Cobalt (III) acetate solution was prepared and its factor was checked according to the method already described.¹

An appropriate solution of platinum (IV) was prepared by dissolving 245.0 mg of chloroplatinic acid (H₂PtCl₆·6H₂O Fering Chemical Works, China) in 300 ml of 2.0 N hydrochloric acid. Quadrivalent platinum was reduced to platinum (II) with copper (I) chloride, the excess of which was oxidized with air and the factor of the solution obtained was checked with permanganate according to the method after Günther et al.⁷

All other chemicals used were either of analytical grade or equivalent purity.

Apparatus: An electronic pH meter (WG Type Model 290) with platinum as indicating and saturated calomel as reference electrodes were used for potential measurements.

Procedure: A definite aliquot (0.5-12.0 ml) of platinum (II) solution, obtained and standardized after the reduction of platinum (IV), as referred above, was transferred to a 100 ml Pyrex glass beaker to which 20 ml of 10N H₂SO₄ were added. Titration was done by adding a definite volume of cobalt (III) acetate