



EXTRACTION- SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM (III) WITH MTPH SOLUTION IN DMF

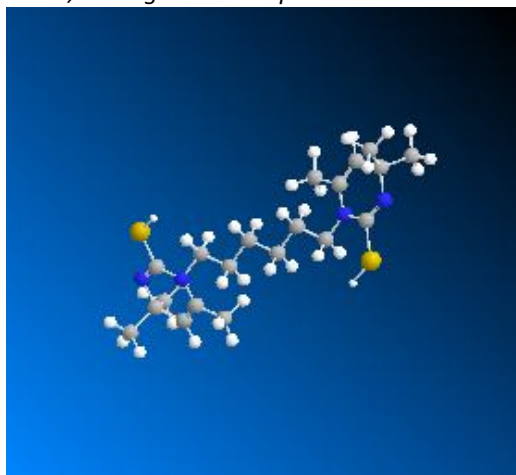
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ABSTRACT

An Extraction of Ruthenium (III) metal by the newly synthesized bis 1,6-(2-mercapto 4,4,6-trimethyl pyrimidyl)-hexane (MTPH) is discussed with its spectroscopic determination. A bidentate ligand that is MTPH is highly sensitive and selective reagent used for Ruthenium metal at the desired acidity of 5M at about boiling water temperature. The Ru(III)-MTPH complex exhibits maximum absorption at 620 nm. The extractant (MTPH) shows significantly high distribution ratio for the Ruthenium metal. It permits separation and determination of Ru(III) from synthetic mixtures corresponding to alloys. The spectrophotometric determination of Ru (III) by using bis 1,6-(2-mercapto 4,4,6-trimethyl pyrimidyl) hexane requires overall 15-20 min.

KEY WORD: Extraction of Ruthenium , boiling water temperature.



Graphical Abstract: bis 1,6-(2-mercapto 4,4,6-trimethyl pyrimidyl)-hexane (MTPH) .

INTRODUCTION

To develop the valuable extractants is an important task for the application of the innovative chemical separation techniques to the reprocessing of the waste water. Ruthenium is widely used in the electronic industry, as one of the most effective hardeners in high-density alloys. Ruthenium alloyed with other platinum metals is used to make an electrical contact for heavy wear resistance materials. Ruthenium and its chloro complexes, have been much used in the catalytic oxidation of some organic compounds. Ruthenium shows resistance to common acids including aqua-regia. It may be electrodeposited from molten salt for electroplating of brass metals. There has been considerable current interest in the chemistry of Ruthenium primarily because of the fascinating electron transfer, photochemical and catalytic properties

obtained by the complexes of this metal. Thus, the widespread application of ruthenium and its compounds in various fields serves as an impulsion for the development of the ruthenium applied analytical chemistry. Selective fast and efficient methods for determination of ruthenium were developed [1-5], Depending on the solution pH, metal ion concentrations in solution, presence of oxidants and reductants as well as their concentration, ruthenium can exist in the form of several complexes, each exhibiting its own catalytic and voltammetric activities [6-8]. In view of the tremendous analytical potential of pyrimidinethiols [9-11], it was thought worthwhile to undertake the synthesis of substituted mercaptopyrimidines and to explore their use as versatile and selective extractive photometric reagents for platinum metals and other base metals. This article reviews the recent developments and technical applicability of various treatments for the removal of heavy metal like Ruthenium from industrial wastewater. A particular focus is given to innovative physico-chemical removal processes such as; adsorption on new adsorbents.

Experimental:

Apparatus, Material and Experimental Method

Absorbance measurements were made on Elico digital spectrophotometer model L-171 with 1 cm. quartz cell. Standard glassware's were used for volumetric measurements. DMF, n-pentanol and other solvents required for the extraction of Ruthenium complex were used after purification. Standard solutions of various cations and anions for diverse ion study on the extraction of Ruthenium complex were prepared by dissolving appropriate quantity of the corresponding salt in double distilled water.

Standard Ruthenium (III) Solution:

A stock solution of Ru (III) was prepared by dissolving 1g Ruthenium chloride (S.D fine chem. Ltd.) in 1M hydrochloric acid and diluted the solution up to the mark in 1000 ml volumetric flask with double distilled water. After standardization of the stock solution [12], it was used to prepare low concentration working solutions of Ruthenium in double distilled water.

Synthesis bis 1,6-(2-mercapto 4,4,6-trimethyl pyridimidyl)- hexane [MTPH]:

MTPH was synthesized in two steps; in the first step 2- methyl -2- isothiocyanato - 4- pentanone (I) was synthesized from – 4 - methyl-pent-3-ene-2-one and ammonium thiocyanate. In the second step bis 1,6-(2-mercapto 4,4,6-trimethyl pyrimidyl)- hexane (II) was synthesized by reacting (I) with 1,6-diamino hexane in alcohol (Scheme)

Step - I

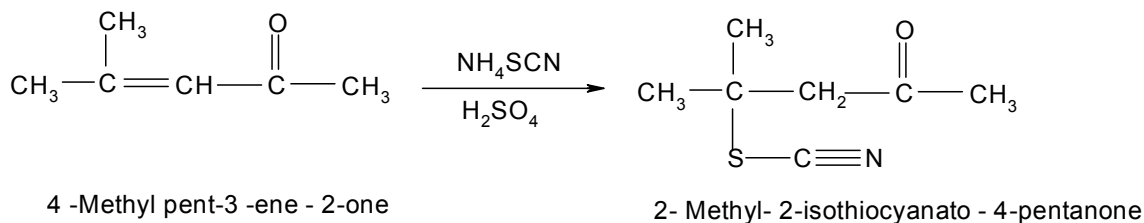


Table 1.1: Spectral Characteristics of Ru (III)-MTPH Complex.

- 1) Ru (III) = 5 to 30 ppm
 2) MTPH = 3 ml 0.1 M in DMF
 3) Blank = Amyl alcohol blank
 4) Heating time = 5 minute
 5) HCl = 5 M
 6) Scan = 500 nm-700 nm

Wavelength nm	Absorbance						Reagent
	Ru (III), ppm						
	5	10	15	20	25	30	
500	0.011	0.130	0.232	0.371	0.441	0.484	0.009
510	0.016	0.144	0.247	0.383	0.456	0.502	0.006
520	0.023	0.161	0.261	0.401	0.469	0.521	0.002
530	0.030	0.174	0.277	0.415	0.483	0.536	
540	0.038	0.185	0.292	0.432	0.501	0.551	
550	0.047	0.199	0.309	0.447	0.513	0.567	
560	0.055	0.212	0.323	0.461	0.527	0.583	
570	0.066	0.220	0.336	0.475	0.544	0.601	
580	0.074	0.231	0.347	0.489	0.561	0.616	
590	0.085	0.244	0.360	0.502	0.574	0.631	
600	0.094	0.255	0.371	0.515	0.587	0.645	
610	0.101	0.264	0.383	0.527	0.600	0.657	
620	0.106	0.268	0.387	0.531	0.604	0.660	
630	0.103	0.261	0.381	0.522	0.601	0.656	
640	0.092	0.243	0.366	0.507	0.583	0.631	
650	0.079	0.229	0.350	0.491	0.561	0.609	
670	0.066	0.217	0.333	0.474	0.543	0.531	
680	0.052	0.203	0.316	0.449	0.521	0.563	
690	0.040	0.191	0.292	0.426	0.503	0.541	
700	0.028	0.178	0.271	0.407	0.491	0.518	

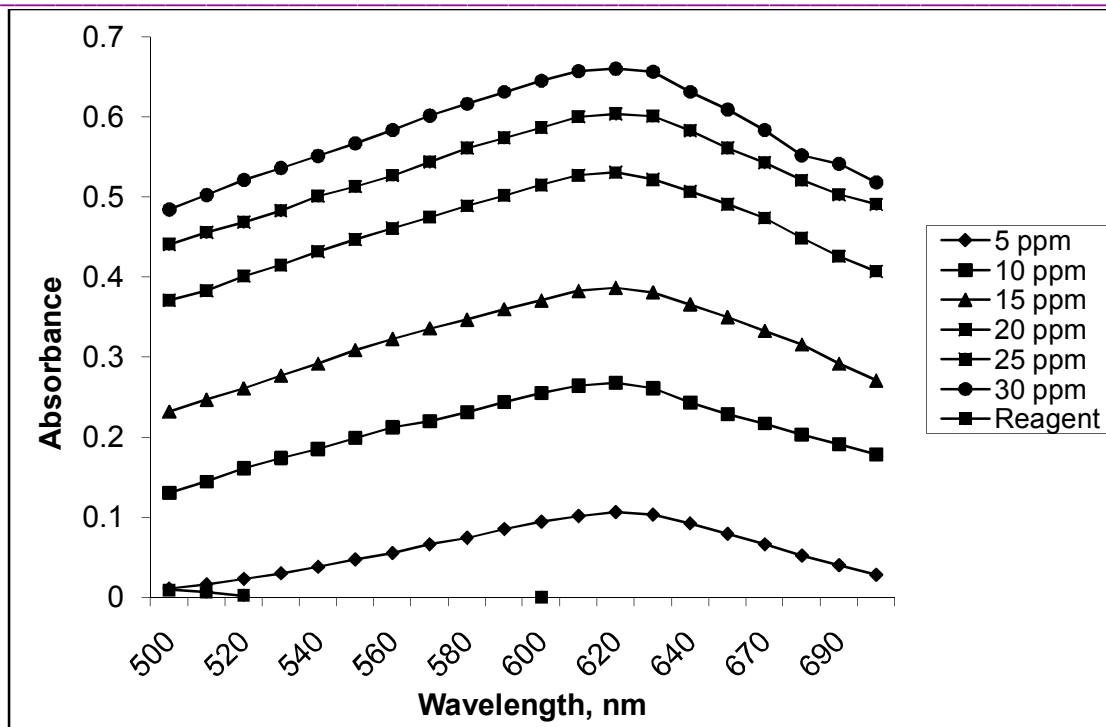


Figure 1.1: Spectral Characteristics of Ru (III)-MTPH Complex.

2. Effect of Acidity

The complete complex formation between Ruthenium and MTPH depends on the acidity of the aqueous phase [13-14]. The optimum acid concentration was determined by using varying amount of hydrochloric acid, 1 M to 10 M, in aqueous phase and 2 ml of 0.1 M MTPH in DMF. The color was developed by recommended procedure and absorbance was recorded at 620 nm by using solvent blank (Table 1.2). Maximum and constant absorbance was obtained between 4.5 M to 6 M HCl. It was also observed that in less or more acidic solution the absorbance decreases. Complexation was not occurred in 8 M and above hydrochloric acid (Figure 1.2). The maximum complexation of Ruthenium with MTPH was not observed in a medium with sulfuric acid, nitric acid, perchloric acid, acetic acid. It was found that maximum complexation of Ruthenium occurred only in hydrochloric acid.

Table 1.2: Effect of Acidity on Ru (III)-MTPH Complex.

1. Ru (III) = 200 μ g
2. MTPH = 2 ml 0.1 M in DMF
3. Blank = Amyl alcohol blank
4. Heating time = 5 minute
5. HCl = 1 M to 8 M
6. λ_{max} = 620 nm

HCl, M	Absorbance
1.0	0.092
2.0	0.123
3.0	0.200
4.0	0.350
4.5	0.475
4.6	0.481
4.7	0.490
4.8	0.516
4.9	0.528
5.0	0.531
5.1	0.526
5.2	0.518
5.3	0.482
5.4	0.470
5.5	0.452
6	0.400
7	0.255
8	0.150

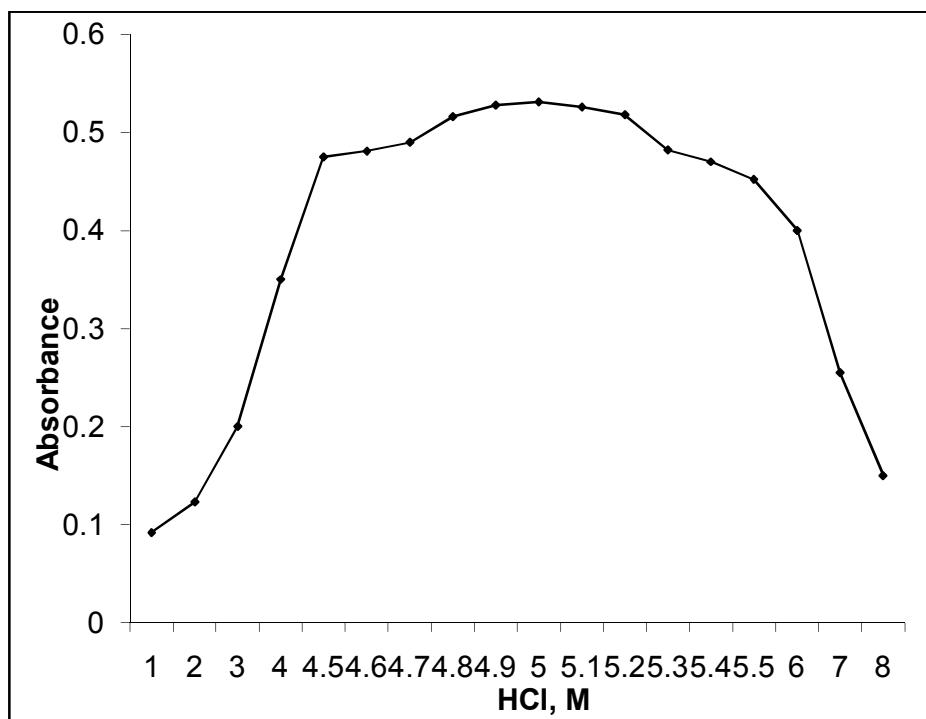


Figure 1.2: Effect of Acidity on Ru (III)-MTPH Complex.

3. Effect of Reagent Concentration

Complexation of Ru (III)-MTPH was also studied by taking different volumes of 0.1 M MTPH solution in DMF. The color was developed as per the recommended procedure and absorbance was measured at 620 nm against solvent blank (Table 1.3). For full color development it was observed that at least 2 ml of 0.1 M MTPH solution in DMF was required (Figure 1.3). There was no effect on complexation of Ruthenium with excess of reagent.

Table 1.3: Effect of Reagent Concentration on Ru (III)-MTPH Complex.

1. Ru (III) = 200 μg s
2. MTPH = 0.2 ml to 4.0 ml of 0.1 M in DMF
3. Blank = Amyl alcohol blank
4. Heating time = 5 min.
5. HCl = 5 M
6. λ_{max} = 620 nm

ml of 0.1 M MTPH in DMF	Absorbance
0.2	0.032
0.4	0.058
0.6	0.112
0.8	0.165
1.0	0.208
1.2	0.255
1.4	0.323
1.6	0.390
1.8	0.436
2.0	0.492
2.2	0.528
2.4	0.528
2.6	0.528
2.8	0.526
3.0	0.528
3.5	0.528
4.0	0.528

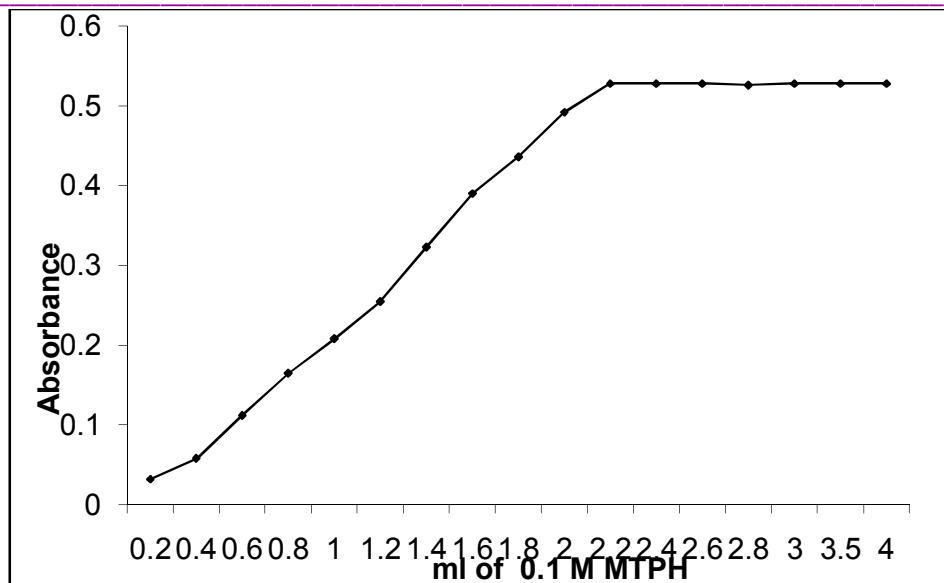


Figure 1.3: Effect of Reagent Concentration on Ru (III)-MTPH Complex.

4. Effect of Heating and Stability of Complex

Heating of the aqueous phase on boiling water bath was required for complete complexation of Ruthenium. The effect of time of heating on the development of full color was studied over a period of 0.5 min to 30 min (Table 1.4). From the result obtained it was found that full color development requires heating of aqueous phase for minimum 3.5 min to 4 min before extraction of complex in amyl alcohol (Figure 1.4). It was also observed that in less or more heating of aqueous phase absorbance decreases.

Stability of complex was also studied by recording the absorbance of the complex with successive intervals of time for 24 h. It was found that the intensity of the extracted complex remained constant for more than 24 h.

Table 1.4: Effect of Heating on Ru (III)-MTPH Complex.

1. Ru (III) = 200 μ g
2. MTPH = 2 ml of 0.1 M in DMF
3. Blank = Amyl alcohol blank
4. HCl = 5 M
5. Heating Period = 0.5 min to 30 min.
6. λ_{max} = 620 nm

Time, min	Absorbance
0.5	0.090
1.0	0.270
2.0	0.368
2.5	0.423
3.0	0.490
3.5	0.525
4.0	0.530
4.5	0.524
5.0	0.520
5.5	0.490

6.0	0.120
10.0	0.050

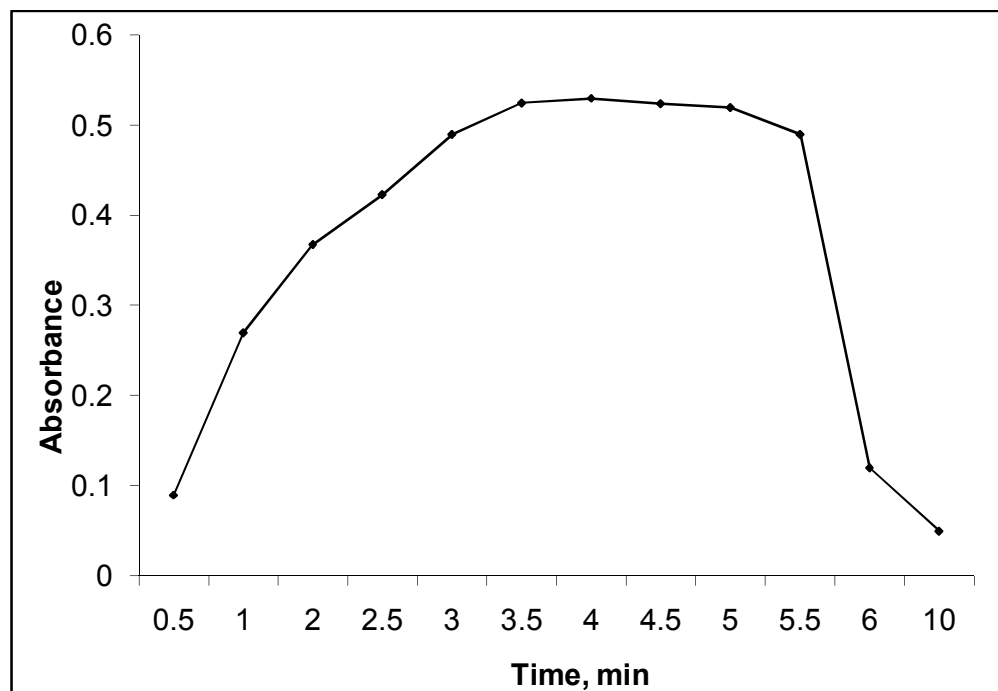


Figure 1.4: Effect of Heating on Ru (III)-MTPH Complex.

5. Effect of Solvent

The extraction of blue colored complex was investigated by using various solvents. Complexation of Ru (III) was carried out as per the recommended procedure. From the result obtained it was observed that maximum extraction occurs only in amyl alcohol, as the highest absorbance of the complex was recorded in this solvent. (Table- 1.5)

Table 1.5: Effect of Solvent on Ru (III)-MTPH Complex.

1. Ru (III) = 200 μ g
2. MTPH = 2 ml of 0.1 M in DMF
3. Blank = Amyl alcohol blank
4. HCl = 5 M
5. Heating time = 5 min
6. λ_{\max} = 620 nm

Solvent	Absorbance
Amyl Alcohol	0.525
Benzene	0.397
Toulene	0.198
Chloroform	0.320
Amyl Acetate	0.221
Chlorobenzene	0.311
Carbontetrachloride	0.267

Methyl iso butyl ketone	0.327
1,2 dichloroethane	0.121
Dichloromethane	0.161

6. CALIBRATION CURVE AND SENSITIVITY

A calibration graph of Ru (III) was prepared by complexing varying amount of Ruthenium i.e. 4 µg to 40 µg with 2 ml of 0.1 M MTPH solution in DMF. The complexation was carried out as per the recommended procedure [15]. The blue colored complex was extracted in amyl alcohol and absorbance was recorded at 620 nm against solvent blank (Table 1.6). Plot of absorbance versus concentration of Ruthenium gave a straight line indicating that Beers range up to 200 ppm (Figure 1.5).

The Sandell's sensitivity of the method [16-17] was found to be 36.23 ng cm⁻² and extinction coefficient was found to be 2.7 x 10³ L⁻¹, mol⁻¹, cm⁻¹.

Table 1.6: Calibration Curve for Ru (III)-MTPH Complex.

1. Ru (III) = 4 ppm to 40 ppm
2. MTPH = 2 ml of 0.1 M in DMF
3. Blank = Amyl alcohol blank
4. HCl = 5 M
5. Heating Period = 5 min
6. λ_{max} = 620 nm

Ru (III), ppm	Absorbance
0	0
4	0.085
8	0.215
12	0.310
16	0.425
20	0.520
24	0.567
28	0.620
32	0.647
36	0.686
40	0.710

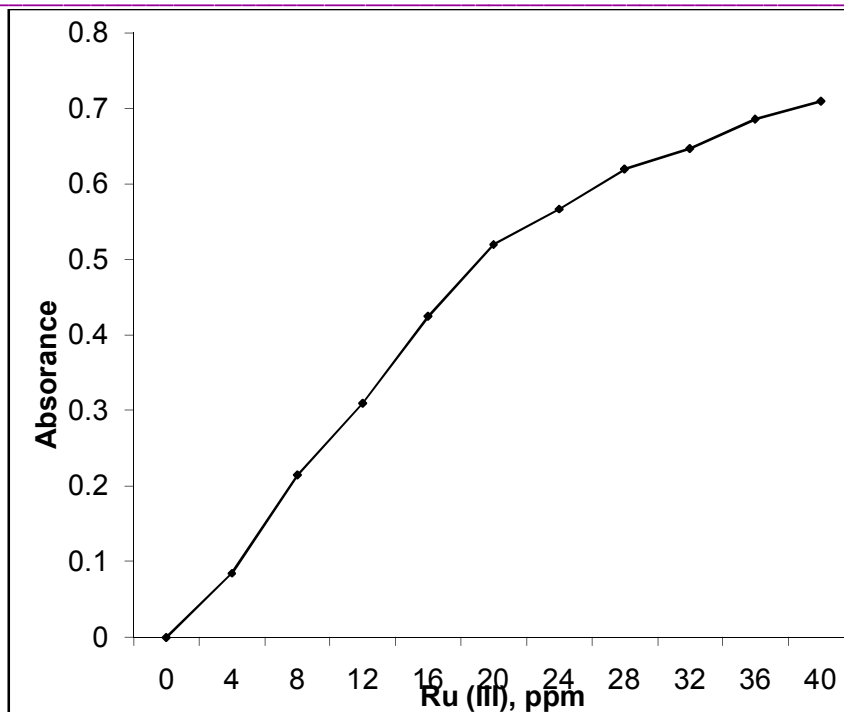


Figure 1.5: Calibration Curve for Ru (III)-MTPH Complex.

7. COMPOSITION OF THE COMPLEX

The composition of the complex could not be determined as the complex is weak and dissociated rapidly when the ligand concentration is less than 100 fold molar excess.

8. EFFECT OF FOREIGN IONS

Under the optimum conditions the effects of various cations and anions on the extraction and spectrophotometric determination of 200 μg of Ru (III) was studied by adding known amount of foreign ion in interest to the Ru (III) aqueous solution before adjusting the required molarity of acid. Complexation was carried out as per the recommended method. In case of intensive interference of some foreign ion the test was repeated with successively smaller amount of the same foreign ion. The tolerance for the added foreign ion was decided as the largest amount that give error less than 2 % in the extractive determination of Ru (III) at 620 nm. The results obtained show that cations like Ni (II), Ga (III), Pd (II), Au (III), Ti (IV), Te (IV), Os (VIII), Fe (II), Pt (IV), W (VI) were tolerated only in lower concentrations. Anions like Thiourea, $\text{S}_2\text{O}_3^{2-}$ and Iodide interfered with extractive determination of Ru (III). (Table- 1.7)

Table 1.7: Effect of Foreign Ion on Extraction of Ru (III)-MTPH Complex.

1. Ru (III) = 200 μg
2. MTPH = 2 ml of 0.1 M in DMF
3. Blank = Amyl alcohol blank
4. HCl = 5M
5. Heating Period = 5 min
6. λ_{max} = 620 nm

Foreign ion added	Amount tolerated, mg
Cr (VI)	10.0
Fe (III)	5.0
Co (II)	10.0
V (V)	5.0
Mn (II)	5.0
Cu (II)	10.0
Zn (II)	10.0
Ni (II)	1.0
Pd (II)	1.0
Cd (II)	10.0
Os (VIII)	0.2
Pt (II)	1.0
Au (III)	2.0
Pb (II)	5.0
Mg (II)	10.0
Ba (II)	10.0
Sn (II)	10.0
Fe (II)	2.0
Ti (IV)	5.0
K (I)	10.0
Na (I)	10.0
Al (III)	10.0
Hg (II)	10.0
Mo (VI)	10.0
Sb (III)	10.0
EDTA	50.0
Salicylate	50.0
Acetate	10.0
Citrate	10.0
Tartarate	10.0
Oxalate	20.0
SCN ⁻	10.0
F ⁻	10.0
Br ⁻	20.0
PO ₄ ⁻⁻⁻	20.0
BO ₃ ⁻⁻⁻	20.0

9. APPLICATION

In order to confirm the usefulness of the proposed method, it was applied for the determination of Ruthenium from synthetic mixtures. The results obtained show that the amount of Ruthenium obtained by the proposed method is in good agreement with the taken values of Ruthenium. (Table- 1.8)

Table 1.8: Synthetic Mixture Analysis.

Composition, μg	Ruthenium (III) Found*, μg	S.D. %
Ru (III) 200, Pt (IV) 100,	198.2	1.1
Ru (III) 200, Ni (II) 100,	198.2	1.1
Ru (III) 200, Ni (II) 100,	198.8	0.6
Ru (III) 200, Cr (VI) 100,	198.8	0.6

* = Average of six determination.

CONCLUSION :

Using bis 1,6-(2-mercapto 4,4,6-trimethyl pyrimidyl) hexane the bidentate ligand, complexation of Ru (III) were studied. Suitable conditions for complete extraction of the above metal ions were determined. This method is highly sensitive and determines above metal ion even in traces amounts.

With the present investigation methods Sandels sensitivity and extinction coefficient found for Ru (III) are 36.23 ng/cm^2 , $2.7 \times 10^3 \text{ l}^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$.

The present method of investigation is also applicable for determination of the Ru (III) from real samples, synthetic mixtures. The values obtained after analysis of real samples, synthetic mixtures are in good agreement with the certified values or taken values.

The spectrophotometric determination of Ru (III) by using bis 1,6-(2-mercapto 4,4,6-trimethyl pyrimidyl) hexane requires overall 15-20 min.

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