

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM (III) USING 2-(5- BROMO-2- OXOINDOLIN-3-YLIDENE) HYDRAZINECARBOTHIOAMIDE AS AN ANALYTICAL REAGENT

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ABSTRACT

2-(5- bromo-2- oxoindolin-3-ylidene) hydrazine carbothioamide, [5-Bromoisatin thiosemicarbazone (HBITSC)] extracts Rhodium (III) quantitatively (99.20%) into n-amyl alcohol. The n-amyl alcohol extract shows an intense peak at 495nm (λ max). Beer's law is obeyed over the Rh (III) concentration range 1.0 – 6.0ug/ml. The molar absorptivity is 3345 dm³ mole⁻¹cm⁻¹ at 495 nm and Sandel's sensitivity is 30.76 ng/cm². The composition of extracted species found to be 1:3 (Rh: HBITSC) by Job's continuous variation and Mole ratio method. Interference by various ions has been studied. The proposed method has been applied for the determination of Rh (III) in synthetic sample.

KEYWORD: HBITSC, Iridium, Spectrophotometry, Molar Absorptivity.

INTRODUCTION

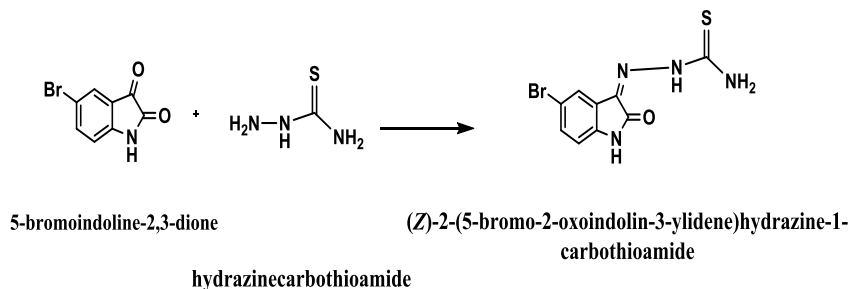
Various reagents^[1-14] are available for the spectrophotometric determination of Rhodium. A solvent extraction is becoming important separation technique in chemistry. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donor atoms and is also used as an efficient analytical reagent in trace analysis of some metal cations.^[1-14] 2-(5-bromo-2- oxoindolin-3-ylidene) hydrazine carbothioamide, [HBITSC] has been used for the development of extractive spectrophotometric methods for the determination of Ni(II)^[8], Pd(II)^[9] and Co(II).^[10] In the present communication, we describe the extractive spectrophotometric determination of Rh(III) with 2-(5-bromo-2- oxoindolin-3-ylidene)hydrazine carbothioamide [HBITSC].

MATERIAL AND METHODS

ELICO - SL 159 spectrophotometer with optically matched quartz or glass cells of 1cm path length were used for absorbance measurements. An ELICO LI-127 pH meter was employed for pH measurements.

Synthesis of 2-(5-Bromo -2-Oxoindolin-3-ylidene)HydrazineCarbothioamide [HBITSC]

Schiff base ligand HBITSC was synthesized by refluxing equimolar amount of ethanolic solution of 5-Bromoisatin with thiosemicarbazide for 4 - 5 hours. On cooling the reaction mixture, a sharp yellow crystal product separated out (80%, yield) which was collected by filtration. The resulting HBITSC was recrystallized using aqueous ethanol as the procedure recommended by Vogel.^[11] The product was characterized by elemental and spectral analysis.



Its solution was prepared in Dimethylformamide (DMF). A stock solution of Rh (III) was prepared by dissolving

appropriate quantity of A.R. grade Rhodium chloride supplied by E. Merck Co. Ltd. in water containing dilute

hydrochloric acid to get 10 mg per cm³ solution of Rh(III). Working solutions of Rh (III) were made by suitable dilutions. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

Extractive Spectrophotometric Determination of Rh (III)

To an aliquot of aqueous solution containing 10.0 to 60.0 µg of Rh (III), 3.0 cm³ of citrate buffer solution of pH 5.5 and 1.5cm³ of 1% solution of HBITSC prepared in DMF was added. Resulting solution was digested for 30 min in boiling water bath. After cooling the volume of solution was made up to 10 cm³ with distilled water and then equilibrated for 1 min with 10cm³ of n-amyl alcohol and the phases were allowed to separate. The n-amyl alcohol extract was collected in a 10 cm³ measuring flask and made up to the mark with n-amyl alcohol. The absorbance of n-amyl alcohol extract was measured at 495 nm against a reagent blank prepared under identical conditions. The Rhodium content of the sample solution was determined from calibration curve. To study the effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH.

Determination of Rh (III) in alloy sample

0.1 to 0.2 gm sample was dissolved in boiling with 10 ml of aquaregia. The resulting solution was evaporated to dryness and the residue was then dissolved in 10 cm³ of 1M HCl, filter, if required and solution was diluted to 100 cm³ with doubly distilled water. The working solution was prepared by appropriate dilution of stock solution. To an aliquot of this solution 1cm³ was analyzed for Rh(III) by the procedure as described earlier.

RESULTS AND DISCUSSION

Rh (III) could be extracted quantitatively (99.20%) by HBITSC into n- amyl alcohol from an aqueous solution of pH 4.0 to 6.2 and in the presence of 3.0 cm³ of buffer solution (citrate buffer) of pH 5.5 and 1.5 cm³ of 1% solution of HBITSC prepared in DMF. Solvents used for extraction of Rh (III) can be arranged on the basis of their extraction coefficient values as n- amylalcohol>n-butylalcohol> ethylacetate>benzylalcohol>chloroform> carbontetrachloride> toluene> nitrobenzene>xylene> chlorobenzene. Here n- amyl alcohol was found to be the best extracting solvent hence; it was selected for the extraction throughout the work "Fig-1" The n- amyl alcohol extract of Rh -HBITSC complex showed an intense peak at 495 nm "Fig - 2". The absorbance due to the reagent is negligible at this wavelength, so the absorption measurements were taken at this wavelength. The result shows that the system confirmed to Beer's law at this wavelength over a Rh (III) concentration range of 1.0- 6.0 µg/ cm³ "Fig -3". The molar absorptivity of the extracted complex on the basis of Rh (III) content was calculated to be 3345 dm³ mole⁻¹ cm⁻¹. It was found that 1.5 cm³ of 1% solution of HBITSC prepared in DMF

was sufficient to extract 60 µg of Rh (III). The colour of the n- amyl alcohol extract was found to be stable at least 36 hrs. at room temperature.

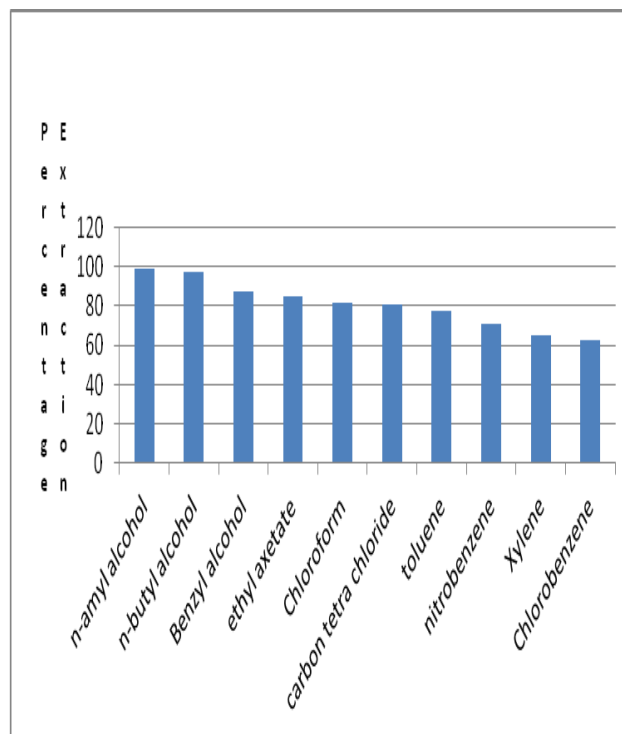


Fig. 1 Percentage Extraction of Rh (III) into Various Organic Solvents

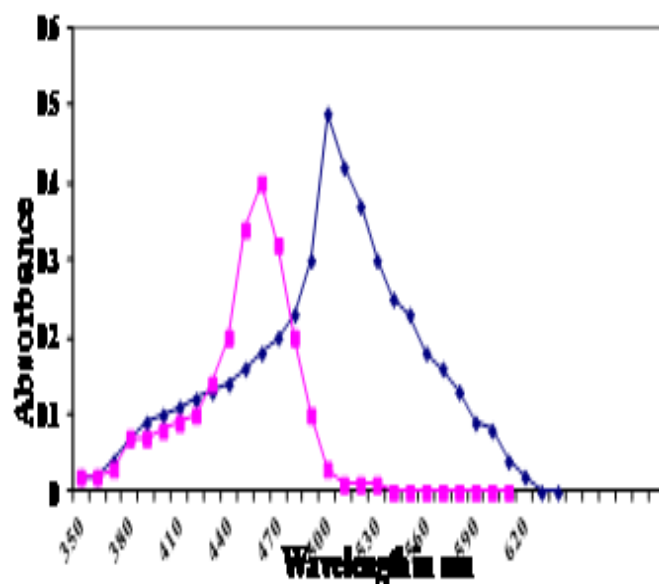


Fig. 2 Solution A: Absorbance spectra of HBITSC
Solution B: Absorbance spectra of Rh -HBITSC Complex

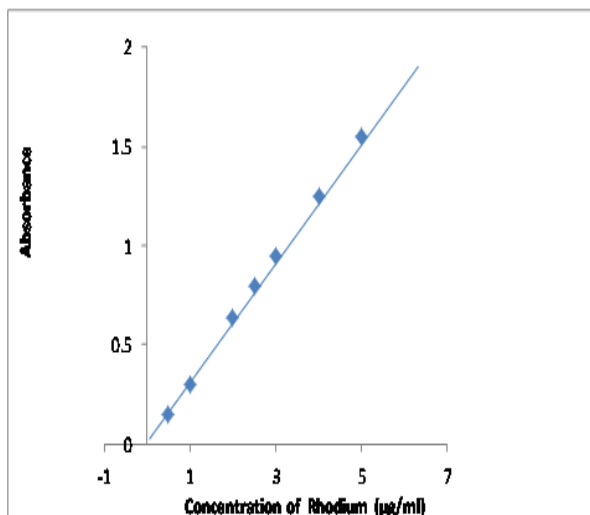


Fig 3 Calibration Curve for Rh (III)

Effect of other ions

Rh (III) (40µg) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Rh (III) (40µg):
 a) 10 mg each of Cd(II), Li(I), Ba (II), Ca(II), Mg(II), Zn(II) and Sr(II)
 b) 0.1 mg each of Ir(III), Pt(IV), Os(IV), Pd(II), Ru(III), Cr(III), Cu(II) and Ni(II)
 g) 20 mg each of - chloride, bromide, nitrate, citrate, thiocyanate, sulphate, persulphate, phosphate and acetate. Interference due to iodide, thiosulphate and EDTA was removed by boiling solution with concentrated HNO_3 before the adjustment of pH.

Composition of the Extracted Complex

The composition of the extracted complex was found to be 1:3 (Rh: HBITSC) by Job's continuous variation and Mole ratio methods. "Fig4 & 5".

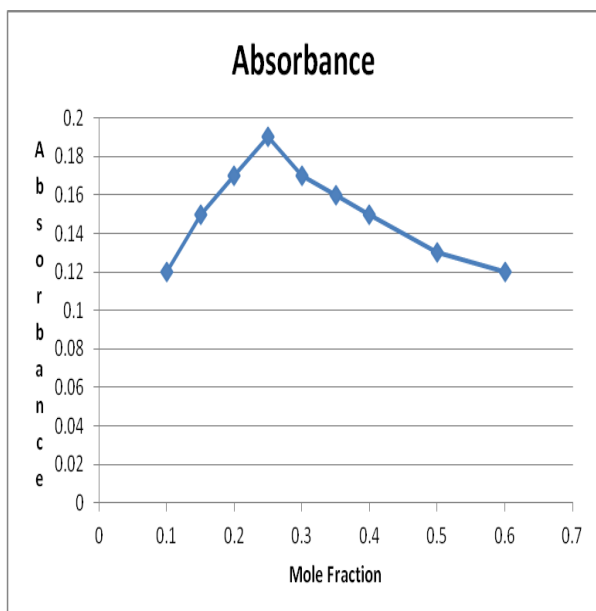


Fig. 4 Job's Continuous Variation Method

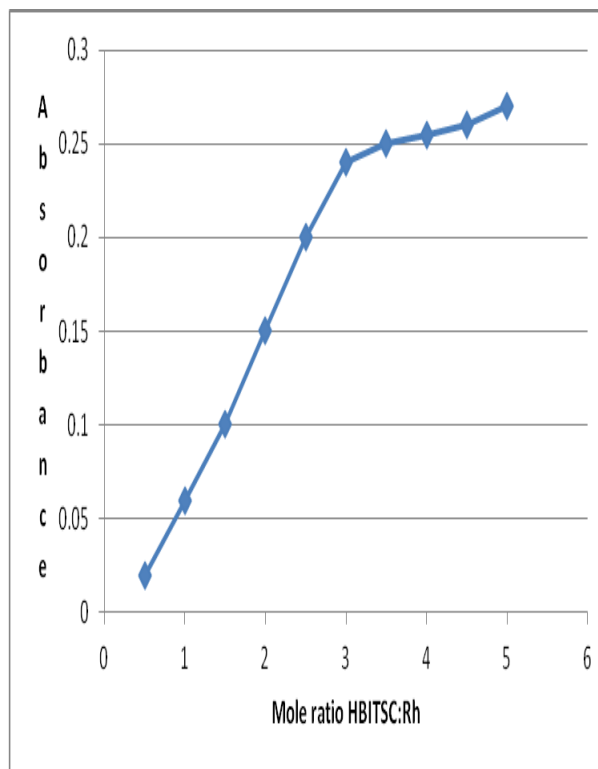


Fig. 5 Mole Ratio method

Precision, Accuracy, Sensitivity and Applications of Method

The precision and accuracy of the method were tested by analyzing the solution containing a known amount of Rh (III) following the recommended procedure. The average of 10 determination of 20 µg of Rh (III) in 10 cm³ solutions was 20.40µg, which is varied between 20.68 and 20.12 at 95% confidence limit. Standard deviation and Sandell's sensitivity of the extracted species is found to be 0.394 and 30.76ng.cm⁻² respectively. The proposed method has been applied for the determination of Rh (III) in alloy sample. The result of the analysis of the sample was comparable with standard method.^[14][Table 1].

Table – 1. Determination of Rhodium (III) in alloy sample

Alloy Sample	Rh(III) found (%) by present* Method	Rh(III) found (%) by standard Method ^[14]
Nickel-Rhodium alloy	5.951	5.948

* Results are the average of three independent determinations.

CONCLUSION

The extractive spectrophotometric determination of Rh(III) was successfully carried out. The method is simple and reliable. Experimental conditions for maximum extraction was determined and applied for the analysis of alloy sample to determine the Rhodium content. The results of the analysis of the sample was comparable with standard method.

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