

Extractive Spectrophotometric Determination of Ruthenium (III) Using 2-(5-Bromo-2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide as an Analytical Reagent

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Abstract: A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Ru(III) by using 2-(5-Bromo-2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide or HBITSC as an analytical reagent. HBITSC has been synthesized and characterized by elemental and spectral analysis. HBITSC extracts Ru(III) quantitatively (99.52 %) into n-amyl alcohol from an aqueous solution of pH range 3.5-5.7 and in the presence of 3 cm³ of acetate buffer (pH 4.6) and 3 cm³ of 1M LiCl. The n-amyl alcohol extract shows an intense peak at 505nm (λ max). Beer's law is obeyed over the Ru(III) concentration range of 1.0-8.0 $\mu\text{g}/\text{cm}^3$. The Sandell's sensitivity and molar absorptivity for Ru-HBITSC system is 10.25 ng/cm^2 and 9855.95L $\text{mole}^{-1}\text{cm}^{-1}$ respectively. The composition of extracted species is found to be 1:3 [Ru: HBITSC] by Job's Continuous Variation and Mole Ratio Method. Interference by various ions has been studied. The proposed method is rapid, sensitive, reproducible and has been successfully applied for determination of Ru(III) in alloy sample.

Keywords: Extractive Spectrophotometry, Ru(III), [2-(5-Bromo-2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide] [HBITSC], Alloy Sample.

1. Introduction

Ruthenium is one of the rarest elements in the Earth's crust. Its abundance is estimated at about 0.0004 parts per million. Ruthenium together with rhodium, palladium, platinum, osmium and iridium forms a group of elements referred to as the platinum group metals (PGM). Ruthenium is the best hardeners for addition to palladium or platinum. Ruthenium compounds are highly toxic and are carcinogenic. Compounds of ruthenium stain the skin, eyes and respiratory tract (mouth, throat, and lungs) very strongly. Ruthenium is mainly used as alloys and as catalysts for industrial processes. Ruthenium-106 is used to treat certain forms of eye cancer.

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 Schiff bases containing nitrogen and other donor atoms and most of them are used as an efficient analytical reagent in trace analysis of some metal cations[1-21]

HBITSC has been used for the development of spectrophotometric method for determination of Palladium (II)[16] and Nickie(II)[17]. In the present communication, we describe the extractive spectrophotometric determination of Ru(III) with

Ru(III), [2-(5-Bromo-2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide or 5-Bromo Isatin thiosemicarbazone] [HBITSC].

2. Material and Methods

All the used chemicals and solvents were of AR grade and were used without further purification and all the solutions were prepared in doubly distilled water.

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

Synthesis of ligand 2-(5-Bromo-2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide [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 crystalline product separated out (80%, yield) which was collected by filtration. The resulting HBITSC was recrystallised using aqueous ethanol as the procedure recommended by Vogel[19]. The product was characterized by elemental and spectral analysis.

Its solution was prepared in Dimethylformamide (DMF). A stock solution of Ru (III) was prepared by dissolving accurately weighed ruthenium chloride in conc. hydrochloric acid by heating on a boiling water bath and the solution was then diluted to 250 cm³ with double distilled water. Its solution was standardized by thiourea method[20]. Working solutions of Ru (III) were made by diluting the stock solution to an appropriate volume. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

Extractive Spectrophotometric Determination of Ru(III)

To an aliquot of aqueous solution containing 10-80µg of Ru(III), 3cm³ of acetate buffer solution of pH 4.6, 3 cm³ of 1M LiCl, and 1 cm³ of 1.0% solution of HBITSC prepared in DMF was added and solution was digested for 25 minutes in boiling water bath. A resulting solution was cooled to room temperature and then volume of solution was made up to 10 cm³ with distilled water and then equilibrated for 1 min with 10 cm³ 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 mark with n-amyl alcohol. The absorbance of n-amyl alcohol extract was measured at 505 nm against a reagent blank prepared under identical conditions. The Ruthenium 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.

1) Determination of Ru (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 ml of 1N HCl filter, if required and solution was diluted to 100 ml with doubly distilled water. The working solution was prepared by appropriate dilution of stock solution. From an aliquot of this solution 1ml was analyzed for Ru (III) by the procedure as described earlier.

3. Result and Discussion

Ru(III) could be extracted quantitatively (99.52%) by HBITSC into n-amyl alcohol from an aqueous solution of pH 3.5 to 5.7(Fig.1). Organic solvents used for extraction of Ru(III) can be arranged on the basis of their extraction coefficient values as n-amyl alcohol > n-butanol > ethyl acetate > benzyl alcohol > chloroform > carbon tetrachloride > xylene > nitrobenzene > toluene > chlorobenzene(Fig.2). n-amyl alcohol was found to be the best extracting solvent; hence, it was selected for extraction throughout the work. The n-amyl alcohol extract of Ru - HBITSC complex showed intense peak at 505 nm. (Fig.3). 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 an Ruthenium concentration range 1.0 to 8.0 µg /cm³ (Fig.4).

The molar absorptivity of the extracted complex on the basis of Ru(III) content was calculated to be 9855.95 L mol⁻¹ cm⁻¹. The Sandell's sensitivity was found to be 10.25 ng/cm². It was found that 1 cm³ of 1.0% DMF solution of HBITSC was

sufficient to extract 80 µg of Ru(III). The colour of the n-amyl alcohol extract was found to be stable at least 48 hrs at room temperature.

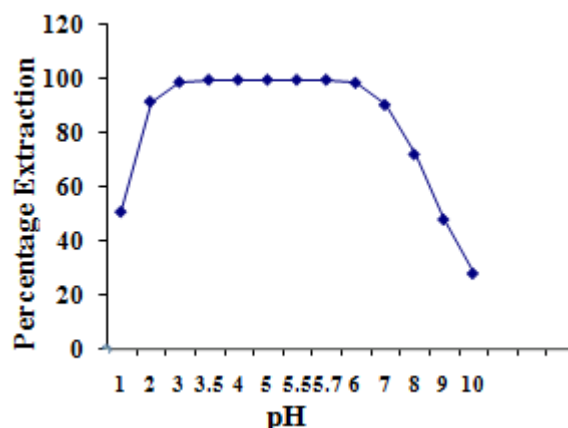


Figure 1: Effect of pH on the Extraction of Ru(III) with ligand 2-(5-Bromo -2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide in n-amyl alcohol

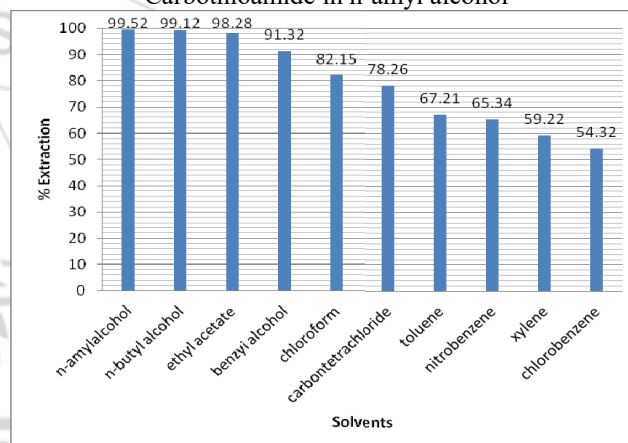


Figure 2: Percentage Extraction of Ru(III) into Various Organic Solvents

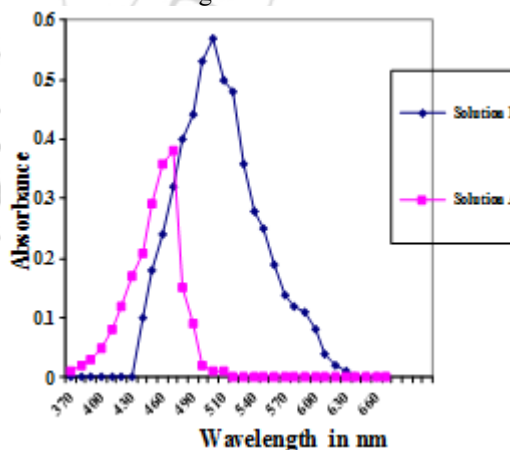


Figure 3: Solution A: Absorbance spectra of HBITSC, Solution B: Absorbance spectra of Ru- HBITSC Complex

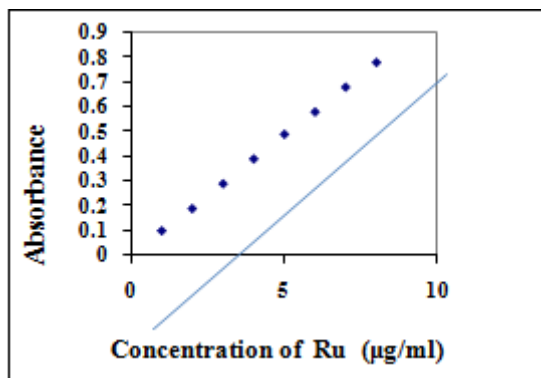


Figure 4: Calibration curve for Ru(III)

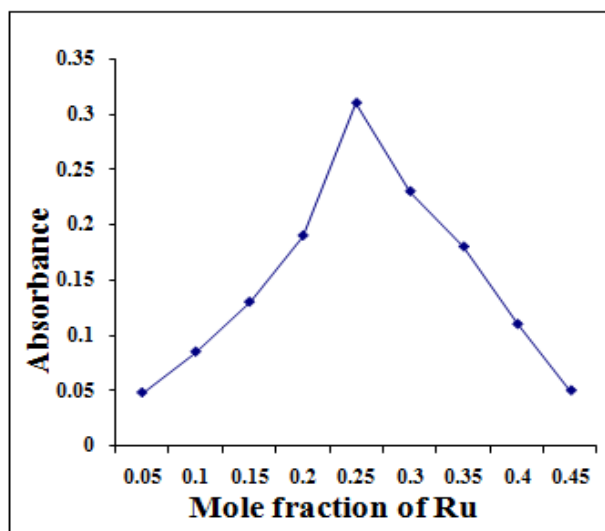


Figure 5: Composition of extractive species Ru:HBITSC by Job's Continuous variation method

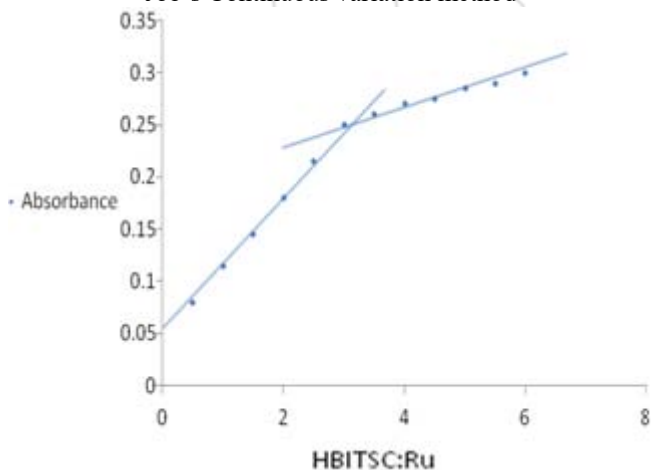


Figure 6: Composition of extractive species Ru:HBITSC by Mole Ratio Method

Effect of other ions

Ru(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 Ru(III) (40µg):

- a) 10 mg each of Li(I), Ca(II),Mg(II), Al(III),Ba(II), Sr(II),Pb(II),Sn(II),Be(II), W(VI),Mo(VI),U(VI) and V(V) .
- b) 5mg each of Zn(II),Hg(II), Ag(I), As(III), Bi(III) and Sb(III).
- c) 2mg each of Mn(II) and Cd(II).

- d) 1mg each of Cr(III), Ce(IV), Th(IV) and Zr(IV).
- e) 0.5mg each of Fe(II), Fe(III) and Ni(II).
- f) 0.1 mg each of Co(II), Pt(IV), Os(IV), Ir(IV), Pd(II) and Cu(II).
- g) 20 mg each of - chloride, bromide, fluoride, sulphate, persulphate, nitrate, phosphate, acetate, oxalate, citrate and tartarate.

Interference due to iodide, nitrite and thiosulphate and EDTA was removed by boiling solution with concentrated HNO₃ before the adjustment of pH.

Composition of the Extracted Complex:

The composition of the extracted complex was found to be 1:3 (Ru:HBITSC) by Job's continuous variation and Mole ratio method (Fig.5 and Fig.6)

Precision, Accuracy, Sensitivity and Application of Method:

The precision and accuracy of the method were tested by analyzing the solution containing a known amount of Ru(III) following the recommended procedure. The average of 10 determination of 10 µg of Ru(III) in 10 cm³ solutions was 10.45µg, which is varied between 10.137µg and 10.763µg at 95% confidence limit and standard deviation was **0.438** **The proposed method has been applied for the determination of Ru(III) in synthetic samples.**

The results of the analysis of the samples were comparable with those obtained by thiourea method[20] for Ru(III) (Table-1).

Table 1: Determination of Ru(III) in alloy sample

Sample	Ru (III) found (%) * Present method	Ru (III) found (%) thiourea method
Titanium Alloy	0.099	0.100

(*Average of three determinations)

4. Acknowledgement

Authors are thankful to the Principal Dr. (Mrs.) J.K.Phadnis, V.E.S. College of Arts, Science and Commerce, Sindhi Society, Chembur, Mumbai – 71 for providing necessary research facilities.

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