



Research Article

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Extractive and spectrophotometric determination of Iridium(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 Iridium (III) quantitatively (99.79%) into *n*-amyl alcohol. The *n*-amyl alcohol extract shows an intense peak at 500nm (λ max). Beer's law is obeyed over the Ir(III) concentration range 1.0 – 6.0ug/ml. The molar absorptivity is 1153.35 L mole⁻¹cm⁻¹ at 500 nm and Sandel's sensitivity is 16.66 ng/cm². The composition of extracted species found to be 1:3 (Ir: 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 Ir (III) in synthetic sample.

Key words: HBITSC, Iridium, Spectrophotometry, Molar Absorptivity.

INTRODUCTION

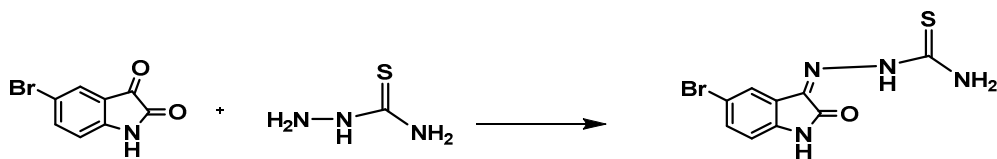
Various reagents [1-15] are available for the spectrophotometric determination of Iridium. A solvent extraction is becoming important separation technique in chemistry. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donor atoms and is also used as an efficient analytical reagent in trace analysis of some metal cations [1-15]. 2-(5-bromo-2-oxoindolin-3-ylidene) hydrazine carbothioamide, [HBITSC] has been used for the development of extractive spectrophotometric methods for the determination of nickel(II)[11] and Palladium(II)[12]. In the present communication, we describe the extractive spectrophotometric determination of Ir(III) with 2-(5-bromo-2-oxoindolin-3-ylidene)hydrazine carbothioamide [HBITSC].

EXPERIMENTAL SECTION

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 [13]. The product was characterized by elemental and spectral analysis.



5-bromoindoline-2,3-dione

(Z)-2-(5-bromo-2-oxoindolin-3-ylidene)hydrazine-1-carbothioamide

hydrazinecarbothioamide

Its solution was prepared in Dimethylformamide (DMF). A stock solution of Ir(III) was prepared by dissolving appropriate quantity of A.R. grade Iridium chloride supplied by E.Merck Co.Ltd. in water containing dilute hydrochloric acid to get 10 mg per cm³. Working solutions of Ir(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 Ir (III):

To an aliquot of aqueous solution containing 10.0 to 60.0 µg of Ir (III), 3.0 cm³ of sodium acetate-acetic acid buffer solution of pH 6.5 and 1cm³ 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 500 nm against a reagent blank prepared under identical conditions. The Iridium 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 Ir(III) in synthetic sample

Synthetic sample of Iridium and platinum was prepared by mixing 9.0 cm³ of 1000 ppm Platinum(IV) and 1.0cm³ of 1000ppm solution of Iridium(III). The resulting solution was diluted to 100 cm³ with distilled water. An aliquot (1ml) of this solution was analysed for Ir (III) by the procedure as described earlier.

RESULTS AND DISCUSSION

Ir (III) could be extracted quantitatively (99.79%) by HBITSC into n- amyl alcohol from an aqueous solution of pH 4.5 to 6.8 and in the presence of 3.0 cm³ of buffer solution (sodium acetate-acetic acid) of pH 6.5 and 1 cm³ of 1% solution of HBITSC prepared in DMF. Solvents used for extraction of Ir (III) can be arranged on the basis of their extraction coefficient values as n- amyl alcohol > n-butyl alcohol > 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 Ir-HBITSC complex showed an intense peak at 500nm [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 Ir(III) concentration range of 1.0- 6.0 µg/ cm³ [Fig -3]. The molar absorptivity of the extracted complex on the basis of Ir(III) content was calculated to be 1153.35 dm³ mole⁻¹ cm⁻¹. It was found that 1.0 cm³ of 1% solution of HBITSC prepared in DMF was sufficient to extract 60 µg of Ir (III). The colour of the n- amyl alcohol extract was found to be stable at least 24 hrs. at room temperature.

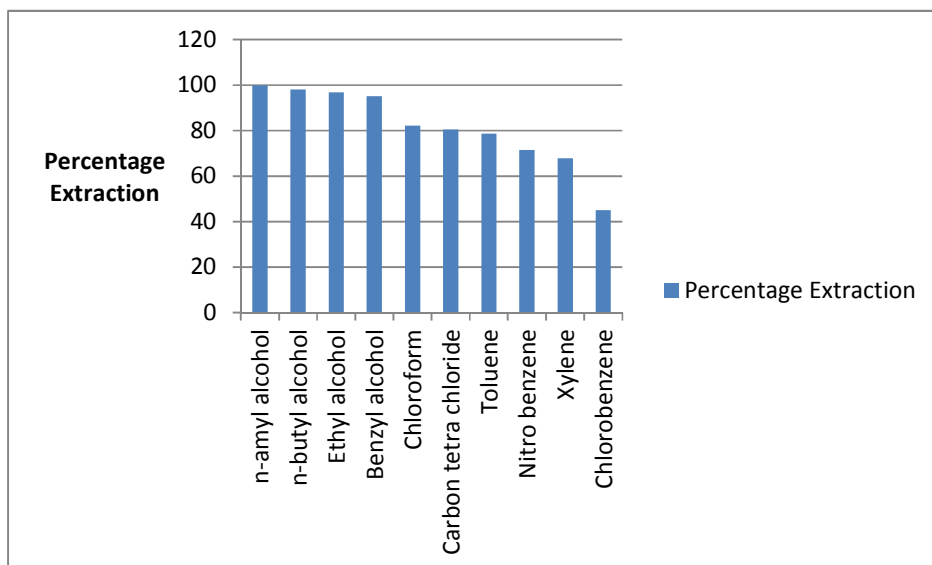


Fig. 1 Percentage Extraction of Ir (III) into Various Organic Solvents

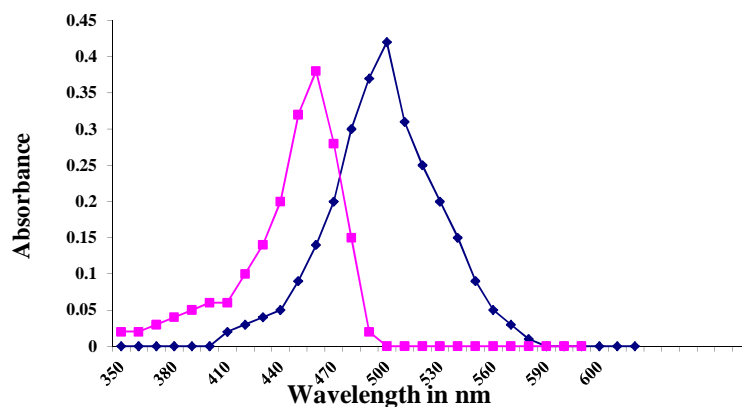


Fig.2 Solution A: Absorbance spectra of HBITSC Solution B: Absorbance spectra of Ir –HBITSC Complex

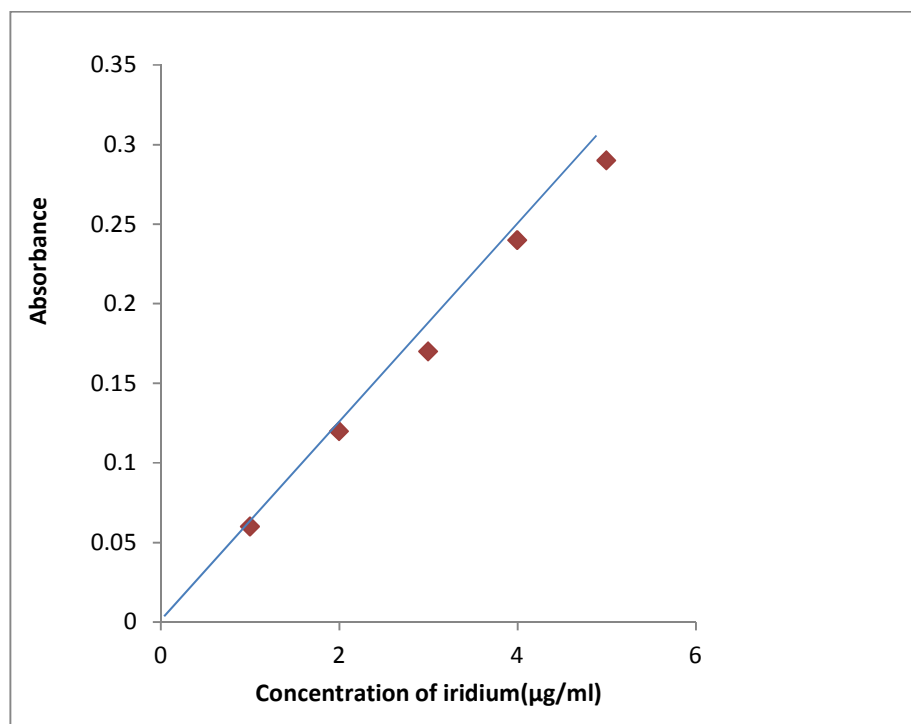


Fig 3 Calibration Curve for Ir (III)

Effect of other ions

Ir (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 Ir(III) (40µg):

- 10 mg each of Cd(II), Li(I), Ba (II), Ca(II), Mg(II), Zn(II) and Sr(II)
- 0.1 mg each of Rh(III), Pt(IV), Os(IV), Pd(II), Ru(III), Cr(III), Cu(II) and Ni(II)
- 20 mg each of - citrate, chloride, bromide, nitrate, thiocyanate and acetate.

Interference due to iodide, 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 (Ir: HBITSC) by Job's continuous variation and Mole ratio methods. [Fig4& 5]

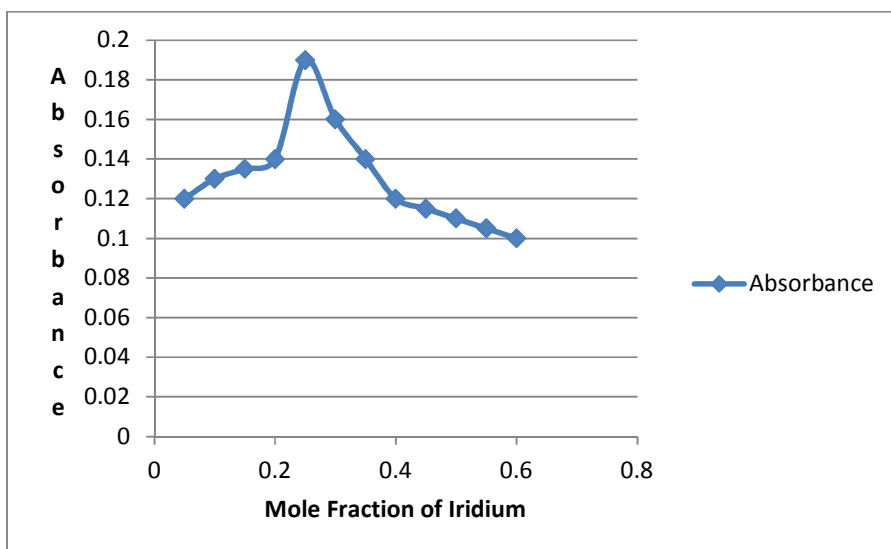


Fig.4 Job's Continuous Variation Method

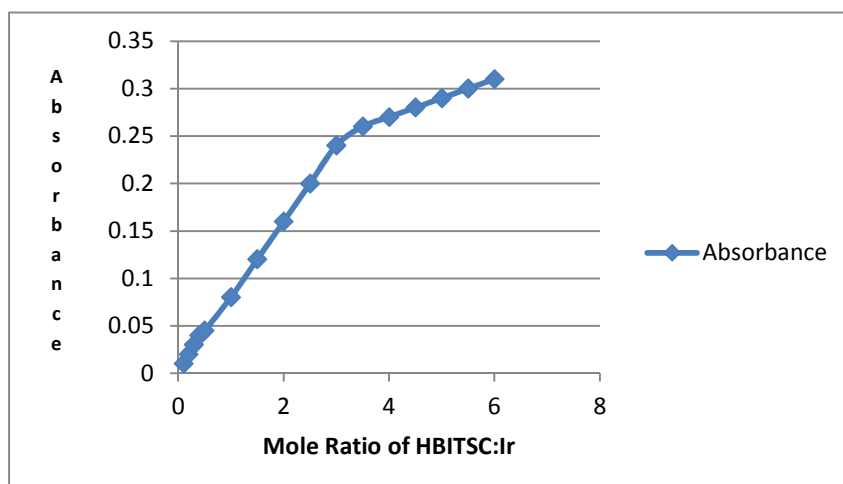


Fig.5 Mole Ratio method

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 Ir (III) following the recommended procedure. The average of 10 determination of 40 μg of Ir (III) in 10 cm^3 solutions was 40.25 μg , which is varied between 40.6358 and 39.8642 at 95% confidence limit. Standard deviation and Sandell's sensitivity of the extracted species is found to be 0.54 and 16.66 $\text{ng}\cdot\text{cm}^{-2}$ respectively. The proposed method has been applied for the determination of Ir(III) in synthetic sample. The result of the analysis of the sample was comparable with reported value [Table 1].

Table – 1. Determination of Iridium (III) in synthetic sample

Sample	Ir(III) found by present Method (μg)	Reported value (μg)
Platinum-Iridium mixture (9:1)	9.995	10.0

* Results are the average of three independent determinations.

CONCLUSION

The extractive spectrophotometric determination of Ir (III) was successfully carried out. The method is simple and reliable. Experimental conditions for maximum extraction was determined and applied for the analysis of synthetic sample to determine the Iridium content. The results of the analysis of the sample were comparable with reported value..

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