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Extractive Spectrophotometric Determination of Osmium (IV) 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 Os(IV) by using 2-(5-Bromo -2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide [HBITSC] as an analytical reagent HBITSC has been synthesized and characterized by elemental and spectral analysis. HBITSC extracts Os (IV) quantitatively (99.73%) into n-amyl alcohol from an aqueous solution of pH range 4.0-5.7 and in the presence of 3cm^3 of phthalate buffer solution of pH 4.5, 3cm^3 of 1M LiCl. The n-amyl alcohol extract shows an intense peak at 565nm (λ max).Beer's law is obeyed over the Os(IV) concentration range of 1.0-8.0 µg/cm^3 The Sandell's sensitivity and molar absorptivity for Os-HBITSC system is 19.0 ngcm^{-2} and 10,000 L mole^{-1}cm^{-1} respectively. The composition of extracted species is found to be 1:2 [Os: HBITSC] by Job's Continuous Variation and Mole Ratio Method. Interference by various ions has been studied. The proposed method is rapid, sensitive and reproducible, has been successfully applied for determination of Os (IV) in synthetic samples.

Keywords: Extractive Spectrophotometry, Os(IV), [2-(5-Bromo-2-Oxoindolin-3-ylidene) Hydrazine Carbothioamide or 5-Bromo Isatin thiosemicarbazone [HBITSC], Samples.

INTRODUCTION

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 [1-27].

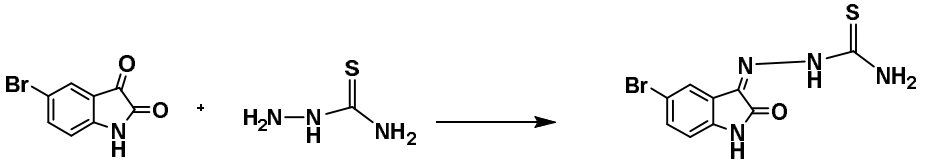
HBITSC has been used for the development of spectrophotometric method for determination of palladium (II) [14] and nickel (II) [15]. In the present communication, we describe the extractive spectrophotometric determination of Os (IV) with HBITSC.

MATERIALS AND METHODS

All the used chemicals and solvents were of AR grade. All 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 h. On cooling the reaction mixture, a sharp yellow crystal product separated out (80%, yield) which was collected by filtration. The resulting H**BITSC** was recrystalised using aqueous ethanol as the procedure recommended by Vogel [25]. The product was characterized by elemental and spectral analysis.



5-bromoindoline-2,3-dione **hydrazinecarbothioamide** **(*Z*)-2-(5-bromo-2-oxoindolin-3-ylidene)hydrazine-1-carbothioamide**

Its solution was prepared in Dimethylformamide (DMF). A stock solution of Os (IV) was prepared by dissolving weighed quantity of ammonium chloro-osmate in double distilled water containing; 1M hydrochloric acid and diluted to the desired volume with doubly distilled water. An aliquot of this solution was analyzed for osmium by thiourea method [27].Working solutions of Os (IV) were made by suitable dilutions.

Extractive Spectrophotometric Determination of Os (IV): To an aliquot of aqueous solution containing 10-80µg of Os (IV), 3cm^{3}of phthalate buffer solution of pH 4.5, 3cm^3 of 1M solution of LiCl and 1 cm^3 of 1.0% solution of HBITSC prepared in DMF was added and solution was digested for 30 minutes in boiling water bath. A resulting solution was cooled to room temperature and then volume of solution was made up to 10 mL with distilled water and then equilibrated for 1 min with 10 cm^3 of n-amyl alcohol and the phases were allowed to separate. The n-amyl alcohol extract was collected in a 10 mL measuring flask and made up to mark with n-amyl alcohol .The absorbance of n-amyl alcohol extract was measured at 565 nm against a reagent blank prepared under identical conditions. The Osmium 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.

Procedure for Determination of Os (IV) in (Osmium alloys): Synthetic sample prepared by mixing Os(IV), Ru(III), Rh(III) or Pt(IV) solution of appropriate concentration then 1cm^3 of this mixture solution was diluted to 100 cm ^{3} with water. 1 cm^3 aliquot of this solution was analyzed for Os (IV) by the procedure as described earlier.

RESULTS AND DISCUSSION

Osmium (IV) could be extracted quantitatively (99.73%) by HBITSC into n-amyl alcohol from an aqueous solution of pH 4.0 to 5.7(Fig.1). Organic solvents used for extraction of Os (IV) 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 Os- HBITSC complex showed intense peak at 565 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 osmium concentration range 1.0 to 8.0 µg /cm^3 (Fig.4). The molar absorptivity of the extracted complex on the basis of Os (IV) content was calculated to be 10,000 L mol^{-1} cm^{-1}.The Sandell's sensitivity was found to be 19.0 ng /cm^2. It was found that 1 cm^3 of 1.0% DMF solution of HBITSC was sufficient to extract 80 µg of Os (IV). The colour of the n-amyl alcohol extract was found to be stable at least 48 h at room temperature.

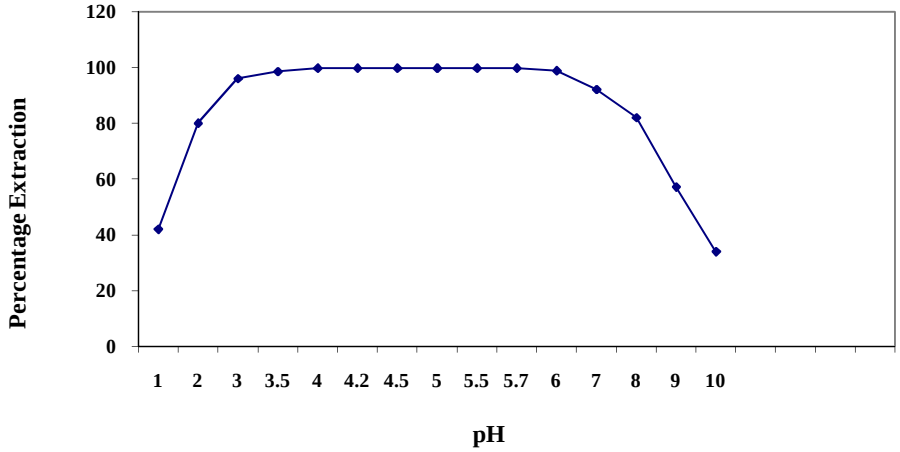


Figure 1: Effect of pH on the Extraction of Os(IV) with 2-(5-Bromo -2-Oxoindolin-3-ylidene)Hydrazine Carbothioamide in n-amyl alcohol

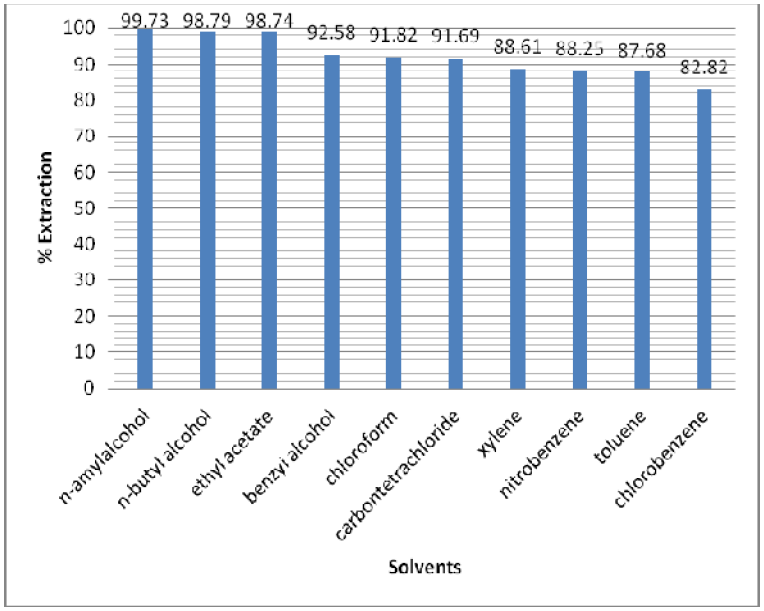


Figure 2: Percentage Extraction of Os (IV) into Various Organic Solvents

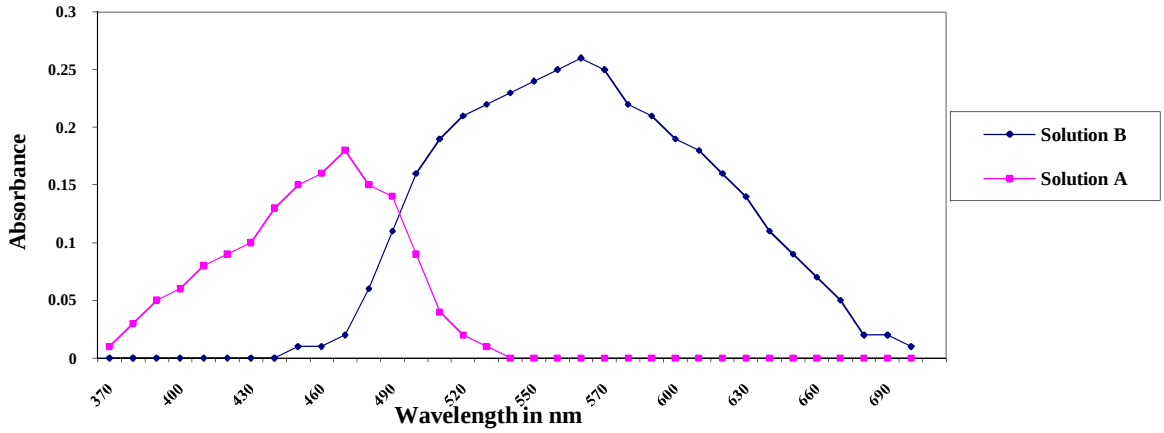


Figure 3: Solution A: Absorbance spectra of HBITSC**,**
Solution B: Absorbance spectra of Os– HBITSC Complex

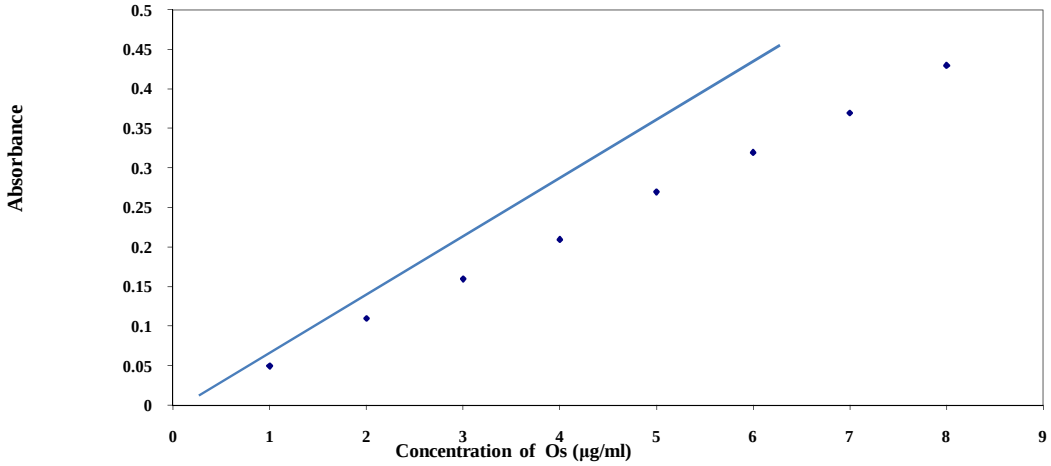


Figure 4: Calibration curve for Os (IV)

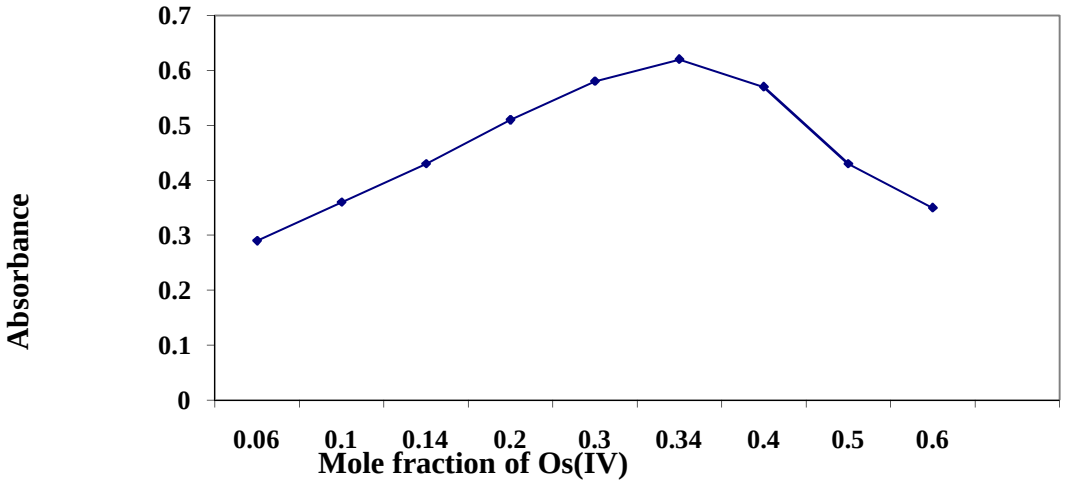


Figure 5: Composition of extractive species Os:HBITSC by Job's Continuous variation method

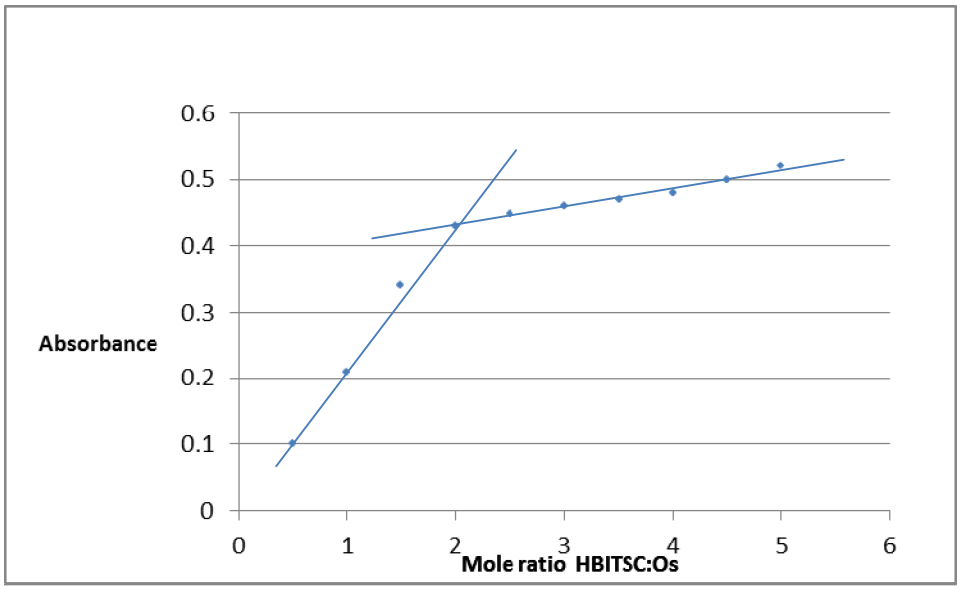


Figure 6: Composition of extractive species Os: HBITSC by Mole Ratio Method

Effect of other ions: Os (IV) (40µg) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Os(IV)(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), Ru(III), 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 HNO_3 before the adjustment of pH.

Composition of the Extracted Complex: The composition of the extracted complex was found to be 1:2 (Os: 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 Os(IV) following the recommended procedure. The average of 10 determination of 30 µg of Os (IV) in 10 cm^3 solutions was 29.85µg, which is varied between 29.608µg and 30.092µg at 95% confidence limit and standard deviation was **0.338.**

APPLICATIONS

The proposed method has been applied for the determination of Os (IV) in synthetic samples. The results of the analysis of the samples were comparable with those obtained by Thiourea method [27] for Os (IV) (Table-1).

Table 1: Determination of Os (IV) in synthetic samples

Synthetic Samples	Os (IV) **found**	
	Present method	**Thiourea method[**27]
Osmium0.1%) (Ruthenium0.1%)(Rhodium0.1%)	0.099%	0.098%
(Osmium0.1%)(Ruthenium0.1%)(Platinium 0.1%)	0.098%	0.097%

*Average of three determination**s**

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