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A NEW DISULPHIDE MOLECULE AS A PHOTOMETRIC REAGENT FOR TRACE DETERMINATION OF OSMIUM

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Disulphide has been used for the spectrophotometric determination of osmium in trace quantities. The complex formed in 1:1 ethanol:water at acidity of 1-5*M* HCl has an absorption maximum at 510nm. The complex is stable for 10hr at room temperature. It obeys Beer's law in the range 2-13ppm of Os(VI) with an optimum range of 2-12ppm. The molar absorptivity and Sandell's sensitivity are $1.49 \times 10^4 l \cdot mole^{-1} cm^{-1}$ and $0.0127 \mu g\ cm^{-2}$ of Os(VI) at 510nm. A large number of metal ions have been tolerated. The stability constant values for the 1:1 complex is 6.55 (log K) and 6.18 (log K) by two different methods at room temperature.

Key Words: Spectrophotometry; Osmium; Disulphide; Stability constant

Introduction

Various methods[1,2] for the trace determination of Osmium have been employed. Although they are more or less sensitive, there are limitations with regard to the oxidation phenomenon and variable reaction conditions specially the state of Os(IV), Os(VI) and Os(VIII). It is well established that even the extraction studies of osmium is accompanied by loss of osmium in the aqueous phase due to selective extraction as well as reduction of osmium cation.

Bismuthiol[3], o-(β-benzoylthiourido) benzoic acid[4], 2-Thiopyrogallol[5] and 4-sulpho-2-aminobenzenethiol[6], have been used for trace determination by photometric methods. Sulphur containing reagents are found to be the most sensitive for osmium.

Reported here is a microchemical technique for trace determination of osmium with a sulphur reagent.

Experimental

A Hilger-Uvispek spectrophotometer was used for absorbance measurements in 1cm glass cells.

A stock standard solution of osmium was obtained by dissolving osmium tetroxide (Johnson & Mathey) in 50ml of 0.2*M* sodium hydroxide and standardised iodometrically[7]. Dilute solution (0.1mg/ml) was prepared from stock by simple dilution.

All chemicals and solvents were all of highest available purity and their solutions were prepared in double-distilled water.

A 0.5% (w/v) ethanolic solution of the reagent, 2,2′-diaminodiphenyldisulphide was used in spectrophotometric studies. The reagent was synthesized by the reported method[8].

Procedure

An aliquot of standard osmium solution (0–100μg) was mixed with 2ml of 0.5% reagent in ethanol in a 25ml flask. To it was added 6.25ml of conc. hydrochloric acid and then 10.5ml ethanol. The solutions are mixed well and the volume is made upto the mark with water. A reagent blank was prepared similarly. But, a solvent blank was found satisfactory. Measure the absorbance of violet osmium complex against solvent blank. Construct a calibration curve and determine the unknown metal concentration.

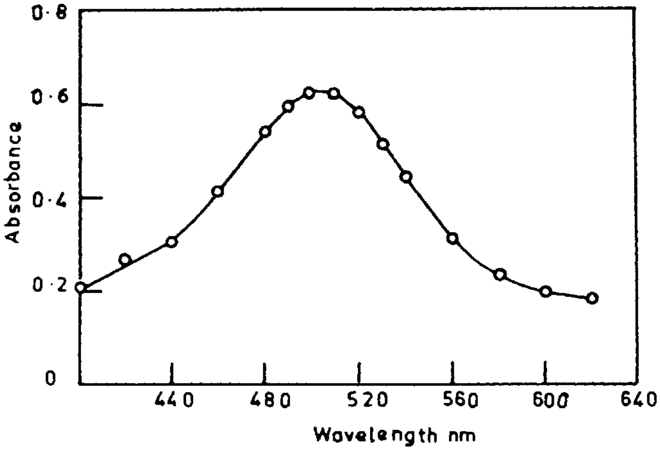

Fig 1 Absorbance curve for 8ppm of Osmium complex against solvent as blank

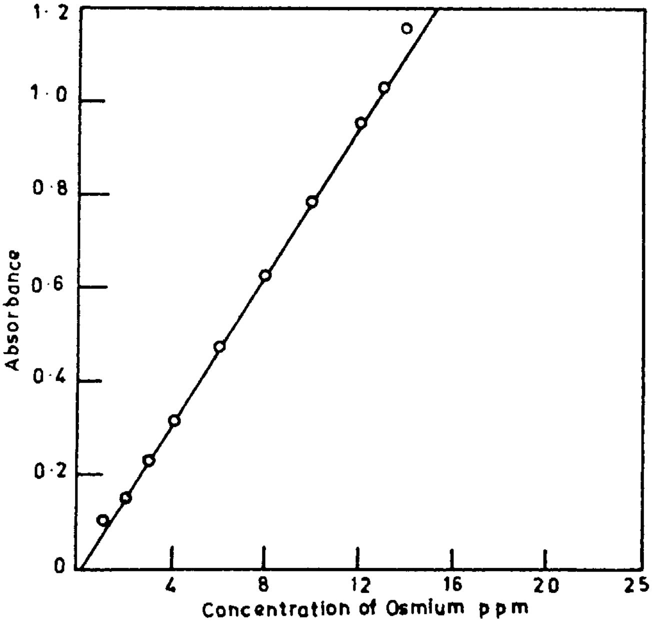

Fig 2 Beer's Law curve for the Osmium complex at 510nm

Results and Discussion

Absorbance Spectra

The spectra of the osmium-disulphide (Os(VI) = $2.104 \times 10^{-5} M$) complex in 1:1 ethanol-water at $3M$ HCl was recorded from 400nm to 600nm (Fig. 1). All measurements were made at 510nm (λ_{max}).

Effect of Acidity, Reagent and Time

The absorbance is constant between $1M$ and $5M$ hydrochloric acid. A $3M$ final acidity was maintained all throughout the measurements for osmium complex at 510nm.

One ml of 0.5% reagent in ethanol was found to be sufficient for full colour development and the range is 1–8ml. 2ml of 0.5% was always used.

The complex system is stable for 10hr at room temperature.

Beer's Law, Optimum Range, Photometric Error, Molar Absorptivity and Sensitivity

The system obeyed Beer's law from 2 to 13ppm of Os(VI) (Fig. 2) and optimum range[8] of determination is 2–12ppm osmium (VI) (Fig. 3).

The percentage relative photometric error per 1% absolute photometric error is 2.22% according to Ayres' plot[10].

The molar absorptivity and Sandell's sensitivity[9] values are 1.49×10^4 l·mole^{-1} cm^{-1} and $0.0127 \mu g$ cm^{-2} of Os(VI) at 510nm.

Interference Studies

The effect of interfering ions were investigated with tolerance limit set at 0.005 scale unit for 4ppm of osmium following the adopted procedure. The method is highly selective in absence of Pd(II), Pt(IV), Cu(II), Fe(III). Table I gives the summary on the limits of individual cations and anions.

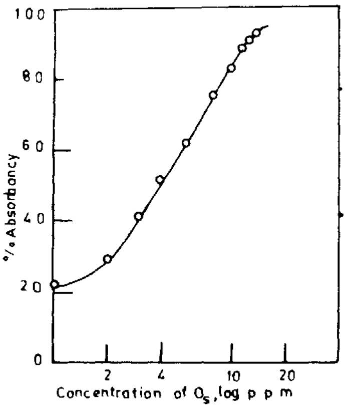

Fig 3 Standard curve for the Osmium complex at 510nm

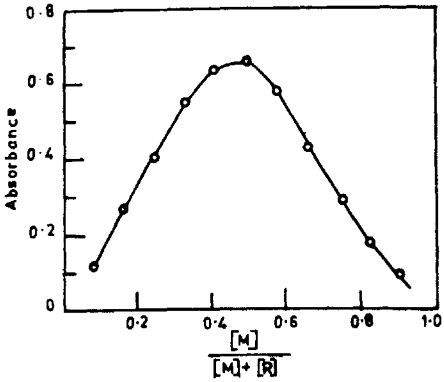

Fig 4 Job's method of continuous variation, metal = 2×10^{-4}M and reagent = 2×10^{-4}M

Table I

Tolerance limits of interfering ions with 4ppm osmium

Ions added	Limits (ppm)	Ions added	Limits (ppm)
Ni(II)	125	Li(I)	75
Cr(III)	400	Mg(II)	250
Mn(II)	50	Sr(II)	200
Zn(II)	75	Tartrate	150
Hg(II)	300	Borate	100
Ca(II)	300	Fluoride	300
Cd(II)	200	Sulphate	
V(V)	8		
Mo(VI)	25		

Composition of the Complex

The reagent: osmium ratio was determined by the method of continuous variation[11] and mole-ratio method[12] with equimolar solutions ($1.6 \times 10^{-5}M$). A composition of 1:1 metal:ligand was found by both the methods (Figs 4 & 5).

Degree of Dissociation and Stability Constant

The stability constant of the Os – R complex was evaluated by graphical extraction and Harvey-Manning's method[13]. The degree of dissociation, α, for the reaction: $ML \rightleftharpoons M + L$ is 0.1378 and log K is calculated to be 6.55.

According to the graphical method given by Chakrabarti[14], K is obtained from the following equation:

$$\lim_{[L]\to 0} \psi = \lim_{[L]\to 0} \frac{\phi - 1}{[L]} = \beta = K$$

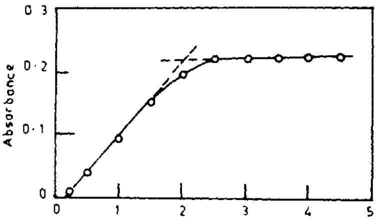

Fig 5 Molar-ratio plot-2ml of metal solution was taken in each case
Metal = Reagent = 2c 10 $^{-4}$M

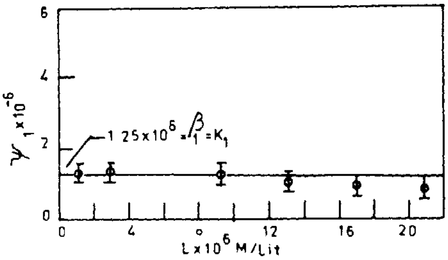

Fig 6 Leden's method. Subsidiary function as a function of the free-ligand concentration L.

The following overall stability constant for osmium complex by this method is found to be log $K = 6.18$ (Fig. 6).

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