Vol. 1, No.4
Summer, 1990

J.Sci.I.R.Iran

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM (VIII) WITH 1-HYDROXY 2-PYRIDINE - THIONE (SODIUM SALT) AS A REAGENT

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Abstract

A spectrophotometric study of osmium (VIII) complex of 1-hydroxy 2- pyridine thione (HPT) is presented. A red-violet complex, Os $(HPT)_4$ is formed in a highly acidic solution, and shows maximum absorbance at 500 nm with molar absorptivity of 5.12×101. mol^{1}. cm^{-1}. Beer's law is obeyed in the range of 3-60 ppm. Sandel's sensitivity of the method is 0.37 μg. cm^{-2} per 0.001 absorbance unit. V (V), Pt (IV), Cu (II), Sn (IV), Cr (VI), and NO_3. interference. To overcome the interference and improve the selectivity, the Os (VIII) as OsO_4 is extracted in CCl_4 and the extracted Os (VIII) is converted to the complex and measured spectrophotometrically. This method reduces the number of interferences to V(V), Pt (IV), and NO_3-. The method offers the advantages of simplicity, speed and high precision. A spot test for the detection of traces of osmium is also presented.

Introduction

Several methods have been proposed dealing with various chromogenic reagents for the determination of osmium [1-5]. A number of procedures are based on the catalytic effect of osmium in a specific reaction [6, 7]. Some of these reagents react slowly with osmium and conditions for obtaining reproducible color are usually empirical.

The sodium salt of I-hydroxy 2-pyridine thione was used for spectrophotometric determination of Fe (III), Pd and turbidimetric determination of Ag [8-10]. In this study, HPT is suggested as a reagent for spectrophotometric determination of osmium (VIII) and its detection by spot test.

This reagent forms an intense red-violet coloration with Os (VIII). The complex shows an absorption maximum at 500 nm, which appears to be a sensitive reagent for the detemination of microgram amounts of osmium (VIII) with the advantages of simplicity, rapid determination in highly acidic solutions and reasonable selectivity.

Key words: Spectrophotometric, osmium, 1- Hydroxy 2- pyridine - thione, Thione

Experimental Section

Reagents: All chemicals used were of analytical reagent grade or better. Triply distilled deionized water was used throughout.

Osmium (VIII) solution: Stock solution of osmium (VIII) was prepared by dissolving 1g sample of osmium tetroxide, from a sealed ampule, in about 100 ml of 0.2 M sodium hydroxide [11] in a glass stoppered flask. The OS (VIII) solution was then diluted to one liter, standardized iodometrically according to a well established method [12].

HPT was obtained from Aldrich Co (USA) and used without further purification. A 0,001 M solution was prepared by dissolving 0.14195 g in 100 ml of triply distilled deionized water.

Apparatus: Absorption spectra were obtained with a Beckman DK-2A UV-visible spectrophotometer using 1-cm glass cells. Absorbances at a fixed wavelength were measured with a Spectonic-70 spectrophotometer.

Recommended Procedures:

a) Spectrophotometric determination of OS (VIII).

1 ml of sample solution or standard containing 30 - 600 μg of osmium (VIII) and 1 ml of 0.001 M of the reagent solution is transferred into a 10 ml calibrated flask and diluted to volume with concentrated phosphoric acid and shaken well. The absorbance is measured at 500 nm against a reagent blank after 10 minutes. The osmium content is calculated from the calibrated curve prepared, in the same way, by using an appropriate amount of standard solution.

b) Spot test detection of Os (VIII): One drop of osmium is put on a spot test plate. One drop of 1% solution of HPT is added followed by two drops of concentrated phosphoric acid and stirred with a glass rod. A red-violet color emerges which indicates the presence of osmium.

Results and Discussion

Absorption spectra: Osmium (VIII) forms a red - violet complex with HPT in highly acidic solution. The complex shows absorption maxima at 500 nm where ligand of Os (VIII) ion do not show any absorption and therefore all measurments are made at 500 nm. The results are shown on Fig 1.

Conditions of Complex Formation

Study on the effect of acidity on complex formation showed that complex formation was best obtained in highly acidic solutions. In this medium, the complex is completely formed in 10 minutes and the absorbance remains constant even after several weeks. Variation of the ionic strength of Os (VIII) solution did not show any change in absorbance. Temperature change also had no effect on the absorbance of the solution.

Calibration Data

The calibration graphs were obtained as described under the Experimental Section. The color system was found to obey Beer's law in the concentration range of 3 to 60 ppm of osmium (VIII). From the straight line, the average molar absorptivity (ε) of osmium complex was calculated to be: 5.12×10^3 1. $mole^{-1}$ cm^{-1}. The Sandel's sensitivity for the determination of Os (VIII) is 0.0379 μg. cm^{-2} per 0.001 absorbance unit.

Composition of the complex

The composition of the complex was established by the continuous variation, mole ratio and slope ratio methods [13-15]. The graph of the mole ratio method presented in Fig 2. The results show that osmium ar ligand combine in a 1:4 ratio in a well defined comple: The formation constant, K_f of the complex w: calculated [16] and found to be 4.22×10^{16}.

Effect of Diverse Ions.

Table 1 shows the effect of various ions on th determination of osmium. These results are effects c 10,000, 5000, and 2500 ppm of diverse ions on th determination of 10 ppm osmium. As it is seen the onl severe interfering cations are: Pt (IV) and V (V). Whe high concentrations of these ions are present th interference effect of all these ions except Pt (IV) and V (V) can easily be overcome by the extraction technique using carbon tetrachloride. One extraction suffices tc complete the extraction of Osmium (VIII) into CCl_4 leaving the interfering ions in the aqueous phase. As indicated, the only ions which cause serious interference are V (V) and Pt (IV) which should be omitted. Common anions such as chloride, fluoride, bromide, sulphate, acetate, perchlorate as well as phthalate and EDTA did not interfere. Only nitrate interferes and should be absent.

This technique can be used for spot test detection of Os (VIII) in concentrations of about 5 ppm where Pt (IV) and V (V) are absent. If the osmium concentration is less than 5 ppm, the complex solution has no visual color, its color develops as concentration of Os (VIII) increases, giving an intense red - violet coloration in concentrations 10 ppm and higher. In concentrations higher than 70 ppm, the color becomes very intense and changes to black.

Table 1. Effect of diverse ions in the determination of 10ppm of Os (VIII).

Ions	Tolerance Limit
	ppm
Co(II), Cd(II), Al(III), Tl(I), Pb(II), Ca(II), Ba(II), Pd(II), Mn(II), In(III), Hf(IV), Zr(IV), Ti(IV), U(VI)	10^4
Ag(I), Mg(II), Ni(II), Cr(III), Te(IV), Ge(IV)	5×10^3
Hg(II),Fe(III), Y(III),Ce(IV),Mo(VI)	
Cu(II), Sn(IV), Cr(VI)	10^3
Pt(IV), V(V)	*10*
Chloride, Bromide, Fluoride, Iodide, Sulphate, Acetate	10^4
Prophosphate, Perchlorate	
Citrate, Oxalate, Tartarate, Phthalate	5×10^3
Nitrate	*10*

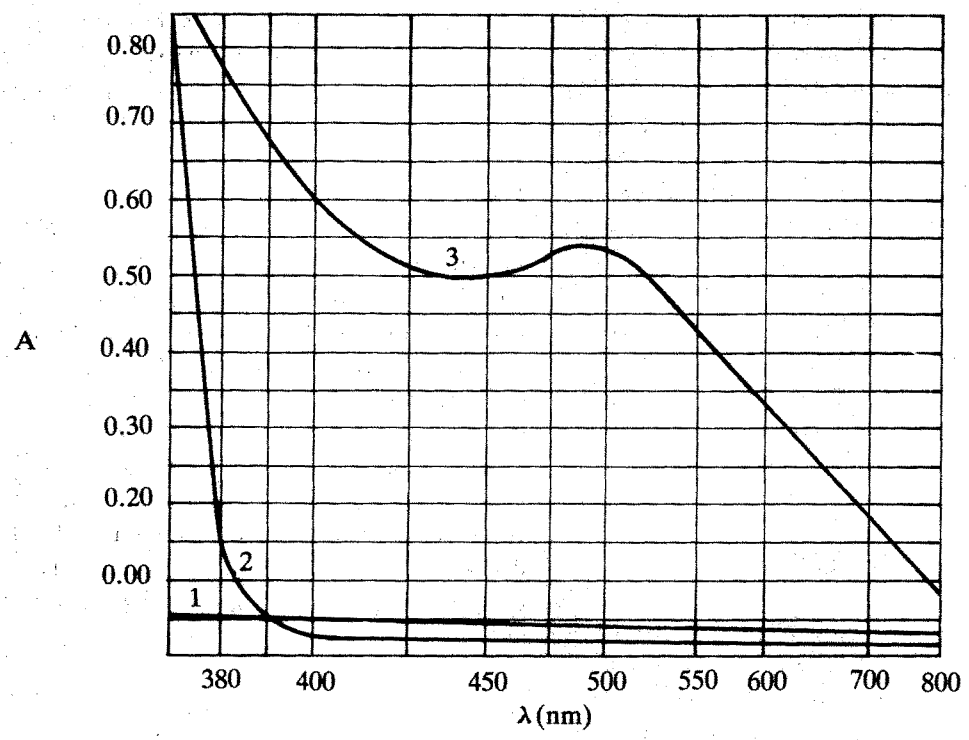

Fig 1. Absorption spectra of: 1. Os (VIII)
2. Thione
3. Complex

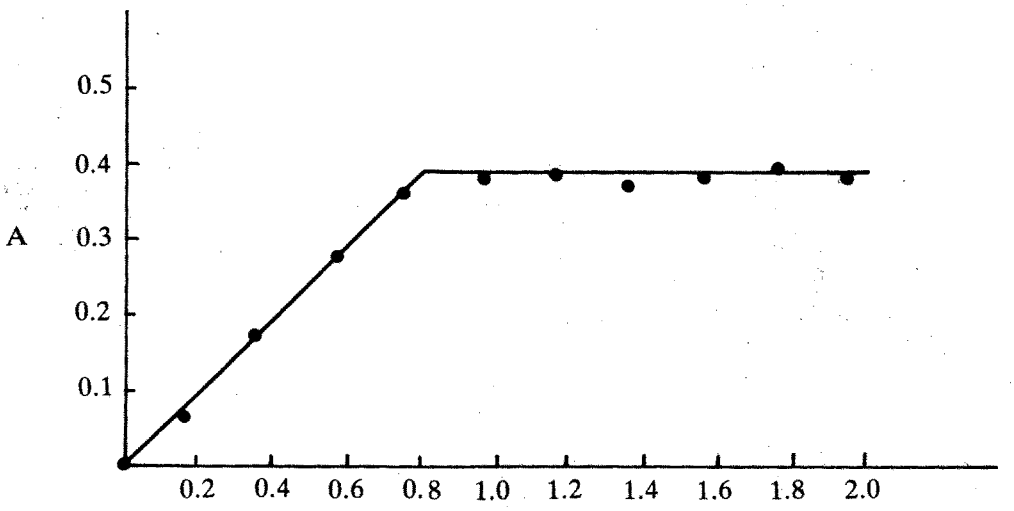

Fig 2. Mole ratio method for osmium-thione complex.

Conclusion

It is shown that thione can be used for spectrophotometric determination of traces of Os (VIII). The proposed method is rapid and simple using a minimum number of reagents and reaction sequences and allows for the determination of Os (VIII) with good accuracy and precision. The method could easily be applied to ores, alloys and catalysts containing small quantities of osmium. The method is recommended for spot - test detection of traces of osmium.

Acknowlegement

The support of Shiraz University Research Council for this work is appreciated.

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