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SPECTROPHOTOMETRIC DETERMINATION OF OS(VIII) WITH NITROSO R SALT AS CHROMOGENIC REAGENT

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ABSTRACT

Several methods have been reported for the spectrophotometric determination of osmium with various chromogenic reagents. Some of these reagents react slowly with osmium and the conditions for obtaining reproductibile colours are usually empirical.

In this context, a simple and sensitive spectrophotometric method for the determination of trace amounts of osmium(VIII) using disodium-1-nitroso-2-hydroxynaphthalene-3,6- disulphonate (Nitroso R salt) is described. The method is based on the formation of an Os–Nitroso R salt complex which exhibits two different colours as function of pH. Linear calibration graphs are obtained up to 60μg/mL of the analyte at pH = 4.8. The stoichiometry of the complex is found to be 1: 4 by mole ratio method. The method is optimized and different analytical parameters were evaluated. For instance, the calculated values for the molar absorptivity are of $3.645.10^3$ L/mol.cm (pH=0; λ= 550nm) and $1.695.10^3$ L/mol.cm (pH=4.8; λ=510nm), respectively. The proposed method should be valuable for the determination of osmium(VIII) with good accuracy and precision.

KEYWORDS: osmium, spectrophotometric determination, Nitroso R salt, chromogenic reagents

1. Introduction

Osmium is the rarest and a trace platinum–group element in the Earth’s crust; it is usually accompanied by many other elements. It is frequently used in small quantities in alloys where frictional wear must be minimized. These alloys are typically used in ballpoint pen tips, fountain pen tips, record player needles, electrical contacts and high pressure bearings. It is therefore not surprising that osmium is no longer considered industrially important, considering this list of applications. A less dated application of osmium is in the platinum/osmium (in a 90:10 ratio) alloy used in implants such as pacemakers and replacement valves. Osmium compounds are used in many processes of organic synthesis. For example, heterometal complexes of osmium with chromium are efficient catalysts of alcohol oxidation, the reaction by–product being only water. Such reactions are promising in the so–called green chemistry [1]. Osmium compounds are used in medical, biological and tomographic studies. There are osmium compounds characterized by antitumor activity. Osmium containing reagents are promising for diagnostics of the presence of specific DNA nucleotide sequences [1].

The quantitative determination of osmium in complex samples usually demands considerable efforts at all stages of the analysis because Os is likely to participate in redox processes and dissolution of the samples can be accompanied by osmium losses as a result of incomplete dissolving and the formation of volatile OsO_4. Unfortunately, the number of spectrophotometric methods providing rapid quantitative determination of osmium in real samples is rather small [1]. Spectrophotometric methods involving organic reagents (Table 1) are often used in the analytical practice, though most of these methods demand complicated sample preparation, e.g. preliminary separation of osmium in the form of tetraoxide, or the extraction of coloured osmium compounds by means of organic solvents. Therefore the search for new accessible, selective and sensitive reagents, which would make it possible to determine the total osmium content, independently of the form of osmium in the analyte, is a very actual task.

Table 1. *Chromogenic reagents for the spectrophotometric determination of osmium*

Reagent	Remarks	Reference
Thiobenzhydrazides	The formed colored complexes are stable for more than 12 hours and their molar absorptivities are in the 10^4 range.	[2]
Ethyl isobutrazine hydro chloride	The reagent reacts with Os(VIII) to form red complex species instantaneously in 2M HCl at 25 ∓ 2^0C	[3]
4– (2-pyridylazo) resorcinol	The orange – red mixed complex of Os absorbs light at λ_{max}= 530nm with a molar absorptivity of $2.5\cdot10^4$ L/mol·cm	[4]
Pyro catechol and hydroxyl amide	An ethanolic solution of pyrocatechol in the presence of hydroxyamide and Os(VIII)on heating at a pH between 7.0 and 9.0 gives a very sensitive color reaction.	[5]
5 – chloro – 2 – hydroxythio benzhydrazide	Beer’s law was obeyed in the concentration range of 1.8 – 14.4 ppm of osmium in a chloroform solution at 510 nm. The molar absorptivity was $1.056\cdot10^4$ L/mol·cm.	[6]
Carminic acid peroxide	The method is based on the osmium catalytic effect on the oxidation of carminic acid by hydrogen peroxide.	[7]
Basic dyes	The catalytic effect on the oxidation reactions on methylene blue, buthylrhodamine B and nile blue by KIO_4 is applied for the determination of Os(IV) in the acidic medium at 90 ∓ 0.5^0C.	[8]
Allyl thiourea	Os(VIII) forms a 1:1 complex with allylthiourea. Conformity to Beer’s law was observed for up to 20µg/mL of osmium in acidic medium (molar absorptivity $2.17\cdot10^4$ L/mol·cm at 298nm)	[9]
Pheno thiazine derivatives	Phenothiazine derivatives readily react with osmium in acid or buffer media to yield colored species which could be followed spectrophotometrically.	[10]
Phenanthren equinone monoxime	Beer’s law is obeyed in the concentration range of 1.0 – 10.9 µg of osmium in 10 mL of chloroform.	[11]
Ethylene thiourea	The method is based on the formation of an instantaneously purple colored complex at room temperature in strongly acidic (pH=1) solution having absorption maximum at 490 nm.	[12]

The first attempts of spectrophotometric determination of osmium using Nitroso R salt as chromogenic reagent have been reported by S. Nath and R.P. Agarwal [13]. Their study was focused on the establishment of the optimum conditions of complex formation and Beer’s law conformity.

Due to the fact that the speciality literature contains litle information regarding the complex formed between osmium and Nitroso - R salt, our aim was to carry out a detailed study on the conditions of this complex formation. In this context, the influence of the solutions pH, heating time and the concentration of ligand and metallic ion have been studied.

2. Experimental research

2.1.Reagents and apparatus

The experiments were performed with:

-Stock solution of osmium of 3mg/mL concentration which has been obtained by the dissolution of OsO_4 in 0.5M HCl. The working solutions were prepared by the dilution of the corresponding amount of the stock solution with bidistilled water at 25 mL.

-The aqueous solution of the Nitroso–R salt (NRS) with a concentration of 10^{-2}M

-The pH adjustments were made with the solutions of HCl, CH_3COOH and CH_3COONa

-The pH values of the solutions were measured with a Radiometer pH M64 pH –meter.

-The absorbance of the solutions was measured on a 104D-WPA spectrophotometer, using glass cells of 1cm.

2.2.Methodology of determination

To a volume of maximum 5 mL of solution containing osmium (0.3-1.5mg) 10mL of Nitroso–R salt solution and 5 mL of buffer acetate(or a determined volume of 2N HCl) were added. Then, the mixture is heating on a bath water, for 2 hours, at boiling. After cooling, the solution is quantitatively passed with bidistiled water into a flask of 25 mL and its absorbance is measured versus a blank sample.

3. Results and discussion

Due to the extraordinary chemical inertness of Os(VIII), the complex with nitroso–R salt is formed only after a continuous heating on a water bath at boiling
the minimum time of heating being of two hours. The complex is stable more than 24 hours.

In the case of Os–NRS complex, the change of absorbance as function of the solution pH (Figure 1) indicates a strong influence of the acidity on this complex formation and stability.

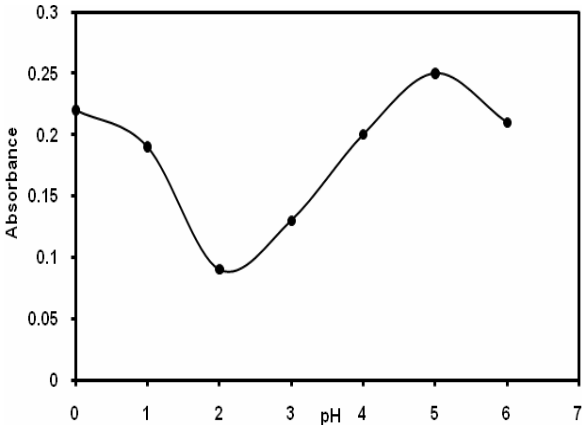


Fig.1. *The effect of the solution pH on the Os–NRS complex (C_{Os}=1.89x10^{-4} mol/L; C_{SRN}= 10^{-2}mol/L).*

According to Figure 1, it is obvious the existence of two ranges of pH in which the Os–NRS complex exhibits different colours. Thus, in hydrochloric solutions (pH=0) a violet color is obtained, while in acetate buffer solutions a green color with the absorption maximum at pH=5 appeared.

In order to study the behavior of the Rh(III) and Os(VIII) mixture, the experiments were performed more in acetate medium.

The absorption spectra of the Os(VIII) complex at pH=0 and pH=4.8, by comparison with that of the Nitroso– R salt reagent are shown in Figure 2.

It can be seen in Figure 2 that the complex spectrum recorded at pH=0 exhibits an absorption maximum at λ=550nm. On the other hand, the spectrum from the acetate medium exhibits two maxima, at λ=510nm and 620nm, respectively.

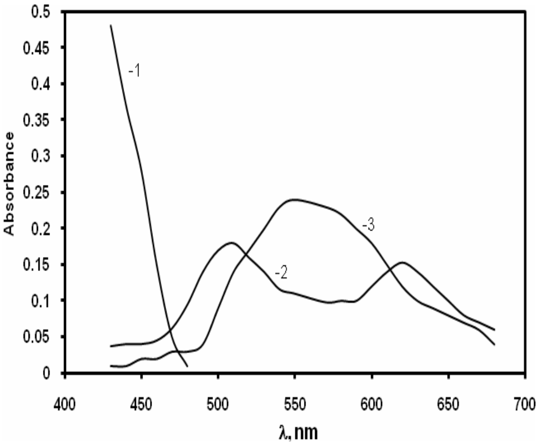


Fig. 2. *Absorption spectra for:*
1- Nitroso-Rsalt reagent; 2-Os-NRS complex at pH= 4.8; 3-Os-NRS complex at pH=0.
(C_{Os}= 1.261x10^{-4}mol/L; C_{NRS}= 10^{-2}mol/L).

In order to establish the linearity range of the absorbance–osmium concentration dependence, the calibration curves were performed at pH=0 and pH=4.8, the absorbance measurements being accomplished at three wavelengths (Fig. 3).

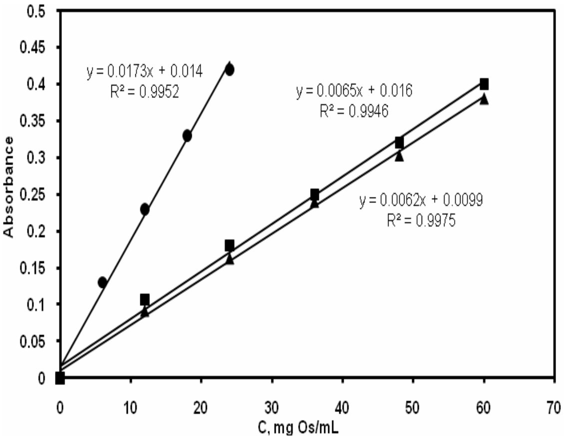


Fig. 3. *The calibration curves at the determination of Os(VIII) with NRS pH= 0, λ= 550nm (●); pH = 4.8, λ= 510 nm (■), λ= 620nm (▲).*

The statistical parameters characteristic to the calibration curves for the spectrophotometric determination of Os(VIII) with Nitroso–R salt as chromogenic reagent are listed in Table 2.

***Table 2**. Analytical parameters*

Reaction medium Parameter	pH = 0 (λ= 550)	pH = 4.8 (λ= 510)	pH =4.8 (λ= 620)
Intercept	0.014	0.016	0.0099
Slope (L/μg)	$0.0173\cdot10^{-3}$	$0.0065\cdot10^{-3}$	$0.0062\cdot10^{-3}$
Correlation coefficient (R^2)	0.9935	0.9946	0.9975
RSD (%)	1.26	2.68	2.70
Linear dynamic range (μg/mL)	6- 24	12- 60	12- 60
Molar absorptivity (L/mol.cm)	$3.645\cdot10^3$	$1.695\cdot10^3$	$1.458\cdot10^3$

The composition of the Os–NRS complex has been established by the mole ratio method. This method involves the variation of the ligand amount, while the amount of metal is keeping constant. The method was applied at pH=0 and 4.8, respectively (Figure 3 and Figure 4).

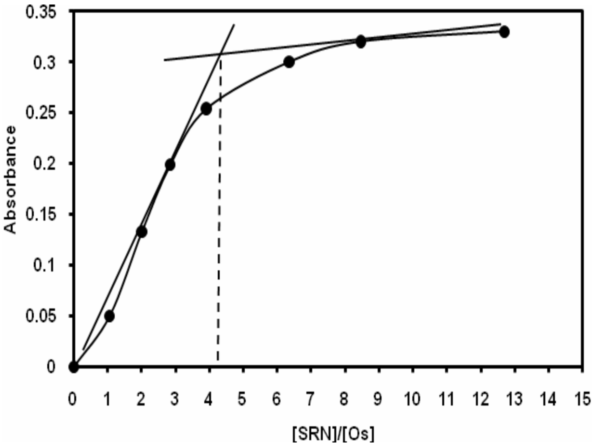


***Fig. 3**. Establishment of the combination ratio for the Os–NRS complex. C_{Os}= 0.1892x10^{-3}mol/L; C_{NRS}- changing ; λ= 510nm; pH = 4.8.*

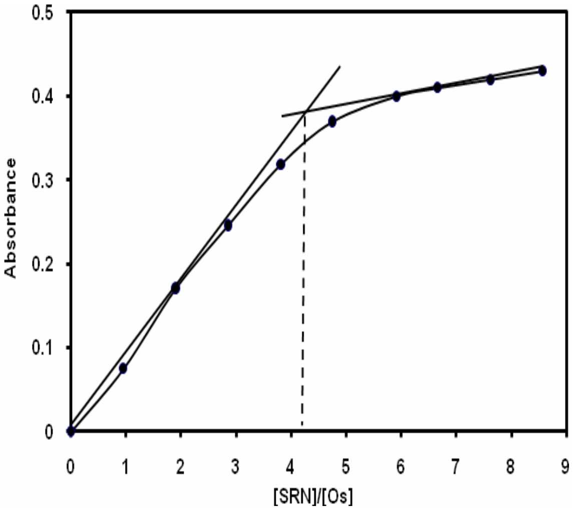


***Fig. 4.** Establisment of the combination ratio for the Os–NRS complex formed in solutions of pH =0 ; C_{Os} = 0.1263x10^{-3}mol/L; C_{NRS}= changing; λ= 550nm.*

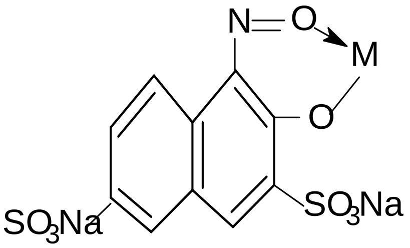
From the analysis of the obtained plots, it is obvious that by the metal–ligand interaction a complex with the combination ratio of 1Me: 4L is formed.

The complex of green color formed at pH=4.8 is characterized by a constant stability with the value of β= 1.5203x10^{15}.

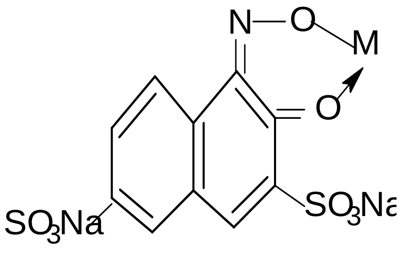
This combination ratio might be due to the fact that in the hydrochloric media OsO_4 is unstable and reduces at low states of oxidation.

According to Losev’s and Kudrina’s research findings [14], as a result of the temperature increasing, in solution is formed the hexachlorosmat (IV) which by interaction with Nitroso–R salt leads to the formation of new Os–O bonds.

The most probable modality of osmium bonding would be the formation of the stable cycles I and II, corresponding to the enolic or cetonic form of the Nitroso–R salt.



(I)



(II)

4. Conclusions

- The complexation reaction between Os(VIII) and Nitroso–R salt depends on the solution pH; the complex may be formed both in acidic medium of pH = 0 (hydrochloric solutions) and at pH 4.8(acetate buffer)
- The products of the reaction are:
  - at pH=0 a complex of violet color having the maximum absorbance at λ= 550nm;
  - at pH=5, a green complex with the maximum absorbance at λ_1=510nm and λ_2= 620nm.
- The calibration curve is linear up to 60μg/mL at pH = 4.8.
- The composition of the Os–NRS complex, established by the mole ratio method, is of 1Os to 4NRS.
- The calculation of the stability complex of the Os–NRS complex leads to the value β= 1.5203×10^{15}.

References

[1]. **D.B. Petrenko, O.A. Tyutyumuk, Yu.M. Dedkov** - *Catalytic kinetic methods for determining osmium(review)*, Inorganic Materials 46(2010) 1493 – 1498.

[2]. **S.C. Shome, S. Nandy, A. Guhathakurta, N.C. Ghosh, H.R. Das, P.K. Gangopadhyay** - *Spectrophotometric determination of ruthenium, rhenium, osmium and platinum with organic thiohydrazides,* Mikrochim Acta 70(1978) 343 – 357 .

[3]. **A. Thimme Gowda, N.M. Made Gowda** - *Spectrophotometric determination of osmium with ethylisobutrazine hydrochloride,* Microchimica Acta 88(1987)351 – 357.

[4]. **S. Dadfarnia, M. Shamsipur** - *Extraction–spectrophotometric determination of osmium using 4–(2- pyridylazo) resorcinol,* Bull. Chem. Soc. Jpn. 64(1991)3063- 3066.

[5]. **M.K. Deb, N. Mishra, K.S. Patel, R.K. Mishra** - *Sensitive spectrophotometric determination of osmium with pyrocatechol and hydroxyamide,*Analyst 116(1991) 323– 325.

[6]. **S.S. Sawant** - *Sequential separation and spectrophotometric determination of osmium and platinum with 5–chloro–2–hydroxythiobenzhydrazide,* Anal. Sci. 25(2009) 813– 818.

[7]. **J.L. Manzoori, M.H. Sorouraddin, M. Amjadi** - *Spectrophotometric determination of osmium based on its catalytic effect on the oxidation of carminic acid by hydrogen peroxide*, Talanta 53(2000) 61– 68.

[8]. **Q.E. Cao, Z.Li, J. Wang, C.Li** - *Catalytic spectrophotometric determination of osmium based on oxidation of basic dyes,* Chem. Anal.(Warsaw) 47(2002) 701–712.

[9]. **B. Morelli** - *Allylthiourea as a reagent for the spectrophotometric determination of osmium,* Analyst 111(1986)1289–1292.

[10]. **J. Seetharamappa, N. Motohashi, D. Kovala–Demertzi** - *Application of phenothiazine derivatives and other compounds for the determination of metals in various samples,* Current Drug Targets 7(2006) 1107–1121.

[11]. **A. Wasey**, **R.K. Bansal, B.K. Puri** - *Spectrophotometric determination of iridium(III) and osmium(VIII) with phenanthrenequinone monoxime after extraction into molten naphtalene,* Microchimica Acta 82(1984) 211 – 220.

[12]. **B. Joseph, S. John, M. Prajila, A. Joseph** - *Spectrophotometric determination of osmium(VIII) in trace amounts using ethylene thiourea(ETU) as chromogenic reagent,* Indian Journal of Chemical Technology 18(2011) 113 -117

[13]. **C. Paduraru** - Ph. D. Thesis „Analitycal Chemistry of Platinum Metals” (2005)

[14]. **V.N. Losev, Yu. V. Kudrina, A.K. Trofimchuk, P.N. Komozin** - *Features of the sorptive extraction of osmium in different states with silica gels chemically modified with mercapto and disulfide groups,* J. Anal. Chem. 59(2004) 546 - 551