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Der Pharma Chemica, 2013, 5(6):241-245
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

New amperometric methods for the trace determination of Os(VIII) with sulphur containing organic acid

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ABSTRACT

Amperometric trace determination of Os(VIII) was successfully carried out with the help of thioglycolic acid at dropping mercury electrode (DME) in 0.5M NaOH medium. The metal to ligand ratio was found to be 5:1. The method enabled the estimation of Os(VIII) solution up to 3.80ppm with maximum error (±2%) in the case of most dilute solutions only. The interference of various ions has also been investigated. The method is found to be fairly selective, sensitive, rapid, precise, accurate and economic.

Keywords: Amperometry, Os(VIII), Thioglycolic acid, 0.1M NaOH

INTRODUCTION

The six metals, named, ruthenium, rhodium, palladium, osmium, iridium, and platinum are called platinum group metals. Osmium metal is lustrous, bluish white, extremely hard, and brittle even at high temperatures. The tetroxide is highly toxic. Very low concentrations in air can cause lung congestion, skin damage or eye damage. Hence there should be some economic technique to estimate low concentration of these metal ions and amperometry is playing a good role in this aspect. Many sulphur containing organic ligands have been used in amperometry for the trace determination of metal ions. Thioglycolic acid (TGA) formulated as $HS\text{-}CH_2\text{-}COOH$ has often been used as a complexing agent and analytical reagent [1-8]. This acid has also been used in grafted onto silica gel [9], in preparation and characterization of glass embedding [10], as potentiometric sensors [11] and in synthesizing nanorods and nanosheets [12]. This ligand has also been exploited earlier for the amperometric determination of some transition metals and non-metals [13, 14]. The present work was undertaken with a view to extend the use of this ligand for the amperometric determination of Os(VIII) in traces at d.m.e.

MATERIALS AND METHODS

All the titrations were performed at d.m.e. vs. S.C.E. using a Toshniwal manual polarograph (Toshniwal India, Model CLO2A). Analytical grade chemicals and doubly distilled water were used. OsO_4 served the purpose of source compound for Os(VIII) TGA solution was prepared fresh daily and standardized. Purified nitrogen gas was employed for deaeration. Limiting current corrected for dilution by the titrant was recorded as a function of the volume of the titrant. Dilution correction was made with the help of equation: $i_{corr} = i_{obs} (V+v)/V$, where i_{corr}, is the corrected current, i_{obs} is the observed current, V is the volume of solution taken initially and v is the volume of titrant added. Null point was obtained graphically taking i_{corr} along y-axis Vs volume of titrant added along x-axis.

RESULTS AND DISCUSSION

Os(VIII) and TGA were polarographically active in 0.5M NaOH medium. Estimation of Os(VIII) could be accomplished with TGA by exploiting the cathodic waves of the metal species or the anodic wave of the organic compound using any of the two organic acids or Os(VIII) respectively as titrant (cathodic and anodic titrations respectively). The null point titrimetric ratio 5:1 was found in case of Os(VIII):TGA in this medium.

TGA was reported [13] to give well-defined one-electron anodic wave in 0.5M NaOH medium. Os(VIII) was observed to give three well defined diffusion controlled waves in this medium as reported by Meites [15]. The diffusion region of the first wave stretched from -0.20V through -0.60V, that of the second wave from -0.85V through -1.40V and that of the third wave from -1.60V. According to Meites the wave corresponded to the reduction scheme:

$$\text{Os(VIII)} \xrightarrow{1^{st}\ \text{wave}} \text{Os(VI)} \xrightarrow{2^{nd}\ \text{wave}} \text{Os(IV)} \xrightarrow{3^{rd}\ \text{wave}} \text{Os(III)}$$

Heights of the successive cathodic waves were in the ratio of 2:2:1.

Titration in this medium (whether cathodic or anodic) gave strong indication of the reduction of Os(VIII) by the organic compounds. This is not surprising in view of the fact that OsO_4 is a known powerful oxidizing agent. It has been reported to bring about oxidation of a similar thio acids like thiomalic acid [16] 2-mercaptopropionic acid [17], 3-mercaptopropionic acid [17] in 0.5M NaOH medium with 5:1 titrimetric ratio, same observed in case of titration with TGA.

Amperometric titrations (cathodic as well as anodic) in this medium were performed at -0.40V and -1.00V. The first titration voltage fell in the limiting regions of TGA as well as Os(VIII) while the second one fell in the limiting region of the second cathodic wave of Os(VIII) alone, any anodic current being totally absent here.

Amperometric curves of the type (a) and (b) of Fig. 1 was obtained when organic compound was used as titrant and those of Fig. 2 was obtained when the metal species was used as titrant. It is very much clear that the reduction current at the null point in these curves given in Fig. 1 obtained at -0.40V is equal to the residual current.

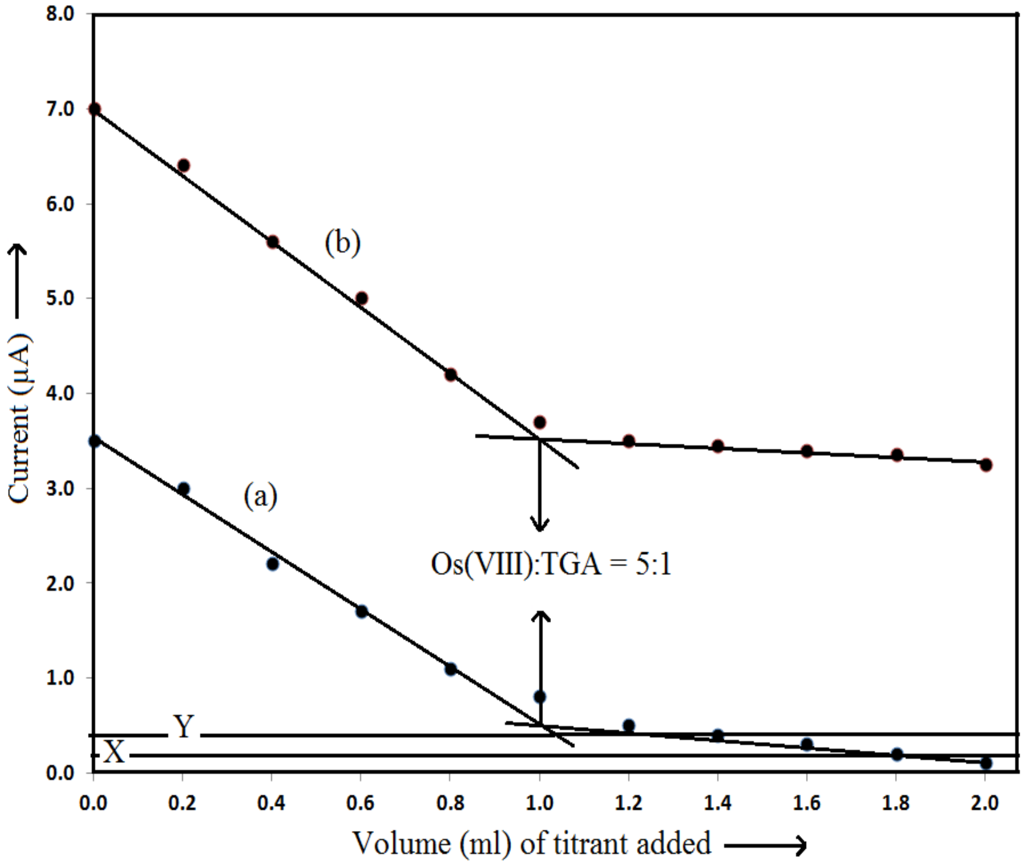

Fig. 1 Amperometric titration curve of Os(VIII):TGA system in 0.5M NaOH medium

Titration voltage : (a) -0.40V
(b) -1.00V
Conc. of Os(VIII) : 0.50mM

Conc. of TGA in the titrant solution : 1.00mM

X = residual current at -0.40V
Y = residual current at -1.00V

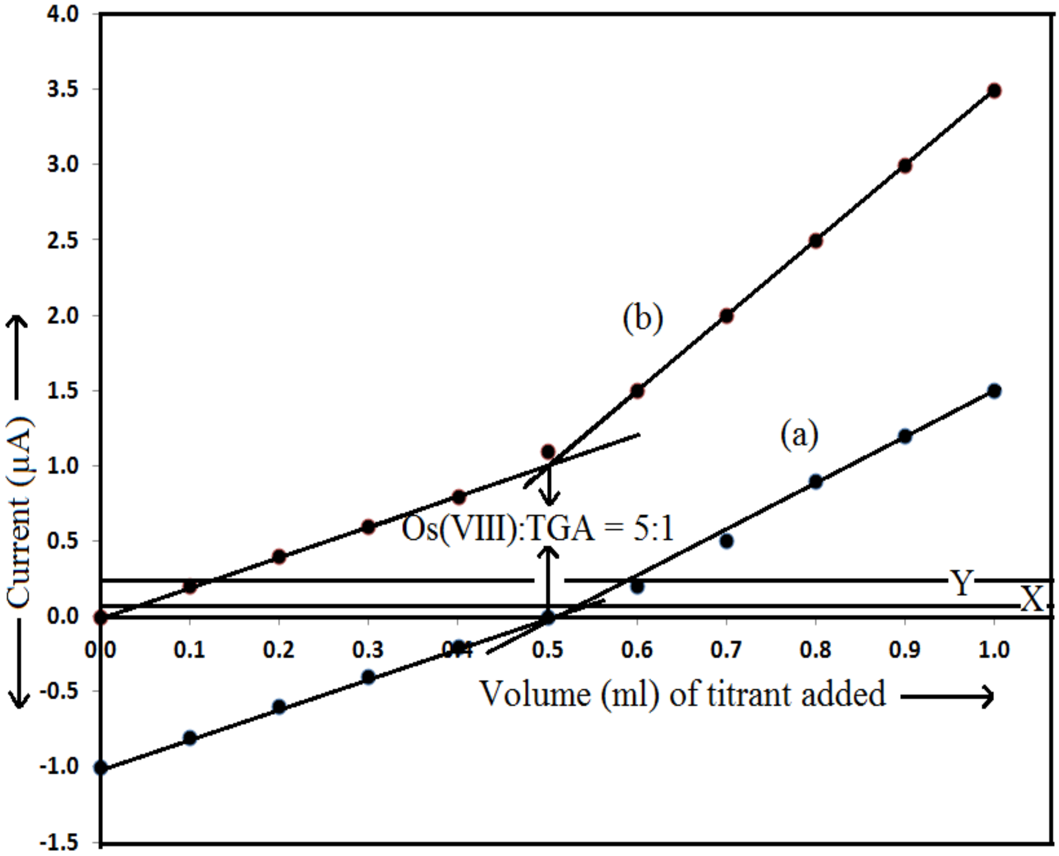

Fig. 2 Amperometric titration curve of Os(VIII):TGA system in 0.5M NaOH medium

Titration voltage : (a) -0.40V
(b) -1.00V

Conc. of TGA : 0.50mM
Conc. of Os(VIII) in the titrant solution : 50.00mM

X = residual current at -0.40V
Y = residual current at -1.00V

Following reaction can be proposed to explain the titrimetric molar ratio 5:1 with TGA:

$$5OsO_4 + HS\text{-}CH_2\text{-}COOH + H_2O \longrightarrow 5OsO_3 + 2HCOOH + H_2S + 2O_2 \qquad (i)$$

Reduction of Os(VIII) to Os(VI) was established from the fact that whenever cathodic titrations were performed at -1.00V in this medium (0.5M NaOH), the diffusion current remained unneutralized at the null point was always equal to that of the second wave of Os(VIII), which is known to appear as a result of electro-reduction of Os(VI) species [18]. On the other hand, titrations at -0.40V always yielded only near zero diffusion current at the null point in this medium. It may be mentioned again that the cathodic current of osmium at this voltage in this medium appears due to the electro-reduction of Os(VIII) to Os(VI) [18].

Other products of the reaction of Os(VIII) with each organic compound embodied in equation (i) were also identified in the 5:1 solution. They can be expected to be arrested in the NaOH medium in the form of HCOONa,

Na_2CO_3 and Na_2S. Presence of formate ion was confirmed by silver mirror test with Tollen's reagent and that of CO_3^{2-} by lime water test. S^{2-} was tested by reacting the solution with HCl and exposing the lead acetate paper to the solution with HCl and exposing the lead-acetate paper to the H_2S vapours thus evolved; the lead acetate paper turned black.

The method evolved is quite efficient and very dilute solutions of Os(VIII) can be estimated with a high degree of accuracy. The solutions as dilute as 3.80 ppm can be measured with reasonable degree of accuracy. Also in each case, cathodic titrations have proved to be more sensitive than anodic titrations. It may be mentioned that these methods are far superior to the thiomalic acid method [16] and comparable to other amperometric methods [17]. The common thiourea method [18] (spectrophotometric) for determination of Os(VIII) is valid over much shorter range of 8-40 ppm only and also suffers, like these new amperometric methods, from interferences from other platinum metals significantly. The new amperometric methods thus have advantage over the spectrophotometric method as far as the determinable range of concentration is concerned.

Checking of interference of foreign ions and selectivity

Study of interference of foreign ions in the new amperometric method was carried out for three concentrations of each metal species: 5.00 mM, 1.00 mM and 0.50 mM. Table-1 includes safe limits of foreign ions in the cell solution. Non-interfering species did not interfere even when present simultaneously in the cell solution. However, for these selectivity tests, the maximum concentration of each species taken was 0.25 mM to avoid super saturation

Table 1 Safe limit of the concentration of foreign ions in the cell solution with respect to the concentration of the metal species

Metal ion	Os(VIII)	
Medium	0.1M NaOH	
Foreign ion	Cathodic titration	Anodic titration
Cl^-	B	B
NO_3^-	B	B
CH_3COO^-	B	B
Ox^{2-}	B	B
WO_4^{2-}	B	B
Mg(II)	B	B
Al(III)	B	B
V(V)	1/10	B
Cr(III)	B	B
Cr(VI)	Equal	Equal
Mn (II)	A	A
Mn (VII)	A	A
Fe(II)	Equal	1/5
Fe(III)	B	B
Co(II)	A	A
Ni(II)	1/10	1/5
Cu(II)	A	A
Zn(II)	A	A
Mo(VI)	1/10	5t
Cd(II)	Equal	1/5
Hg(II)	1/10	1/5
Au(III)	A	A
As(III)	1/20	1/10
SCN^-	B	B

A = serious interference even when the conc. of foreign ion is 1/20 of the metal
B = no interference even when foreign ion is 20 times that of metal

CONCLUSION

The study shows that thioglycolic acid is suitable for the determination of trace quantities of Os(VIII). The methods give reproducibility with standard deviation of 0.05 only. The techniques have the added advantages for the developing country like India in being relatively quick, cheap and simple.

Acknowledgement

The Authors are grateful to Head of the Department of Chemistry, M.D.University, Rohtak for providing facilities for research work.

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