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Amperometric Trace Determination of Se (IV) and Se (VI) using Thioglycolic Acid

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ABSTRACT

Amperometric determination of Se(IV) and Se(VI) were successfully performed with the help of thioglycolic acid at d.m.e. Acetate buffer of pH 4.99 has been employed as a supporting electrolyte for both Se(IV) and Se(VI). Titration potential was selected in the limiting region of anodic wave of thioglycolic acid (TGA) and metal ion solutions were used as titrant, M:L titrimetric ratios have been found to be 1:2 for both Se(IV) and Se(VI). In amperometric titrations, the change in the concentration of substance giving limiting current can be followed through the change in its current. The potential is carefully selected and kept constant throughout the titration. The limiting current was measured after each successive addition of the titrant and the end point is determined graphically. All the titrations were performed at room temperature. Amperometric determination of any solution of a particular strength was carried out at least thrice and concentrations of various metal species determined amperometrically have been given in ppm. Solutions as dilute as 7.9 ppm of the metal ions were estimated with high degree of accuracy. Interference of different foreign ions in the new amperometric method has also been investigated.

Keywords: Amperometry, Se(IV), Se(VI), Thioglycolic acid, Acetate buffer, 1:2.

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INTRODUCTION

Amperometry being simple and low cost technique is very suitable for developing country like India. This technique is employed for the quantitative determination of various metal ions in laboratories and chemical industries etc. It is also used in optimization and characterization of biosensors [1] in pharmaceutical formulations [2] micromolar determination of sulphur oxoanions[3], in binding assay for drug screening[4].

Many sulphur containing organic ligands have been used in amperometry for the trace determination of metal ions. Organic sulphur compounds containing -SH group are also known to give anodic wave at d.m.e.[5-10]. Thioglycolic acid (mercaptoacetic acid) formulated HSCH_2COOH and abbreviated as TGA in this report has often been used as a complexing agent[11-13] and an analytical reagent[14-17]. This acid has also been used in grafted onto silica gel[18], in preparation and characterization of glass embedding [19]. However its capacity to act as an amperometric reagent has by and large remained unexplored. The present work was undertaken with the view to evolve new amperometric methods for estimation of Se (IV) and Se(VI).

EXPERIMENTAL

All the titrations were performed at d.m.e. vs. S.C.E. employing a manual polarograph (Toshniwal India, Model CLO2A). Only analytical grade chemicals and doubly distilled water were used. Agar agar salt bridge containing KCl was used with S.C.E. Titrations were accomplished in 10.0ml of the solution in the cell using different supporting electrolyte. The nitrogen gas was passed for 30 minutes in the beginning of the experiment. The gas also passed for 3-5 minutes after every addition of titrant. This served the purpose of homogenizing the cell solution as well as deaerating the new aliquot of the liquid added. Limiting current corrected for dilution by the titrant was recorded as a function of the volume of titrant. Dilution correction was made with the help of the equation: $i_{\text{corr}} = i_{\text{obs}} (V+v)/V$, 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. The selected e.m.f. was kept constant throughout. Null point was obtained graphically taking i_{corr} (along y-axis) Vs volume of titrant adding along x-axis. Sodium selenate (Na_2SeO_4), Selenious acid (H_2SeO_3) were used as source compound for Se(IV) and Se(VI) respectively. Stock solutions of these compounds were standardized amperometrically [20].

RESULT AND DISCUSSION

Thioglycolic acid is known to give a reversible one electron anodic wave in 0.2F HOAc, 0.2F NaOAc medium [21], $E_{1/2}$ being -0.26V . Similar wave was obtained in acetate buffer of pH 4.99 with $E_{1/2} = -0.26\text{V}$. However, Se (IV) and Se(VI) didn't give any wave in this medium. Amperometric titrations were carried out keeping the potential fixed at -0.10V in the anodic limiting region of TGA. Se(IV) and Se(VI) solutions were used as titrant.

Amperometric curves of upside-down L-shape were obtained and the null point corresponded to metal to ligand titrimetric molar ratio of 1:2 for both Se(IV) and Se(VI) in fig. 1 and 2 respectively. The method enabled the estimation of selenium solution in the

concentration range of 395 ppm to 7.9 ppm for both Se(IV) and Se(VI) species. No colour change was observed during titrations. Details of amperometric results have been given in table-1. Maximum error ($\pm 2\%$) was encountered in case of most dilute i.e. 7.9 ppm solution of selenium.

Table 1: Amperometric Estimation of Se (IV) and Se (VI)

Metal ions	Medium	Anodic limiting region of the ligand wave (-E)	Titration potential selected (V)	Concentration range of metal ion estimated (ppm)
Se(IV)	Acetate buffer of pH 4.99	0.05-0.20	-0.10	395 to 7.9
Se(VI)	Acetate buffer of pH 4.99	0.05-0.20	-0.10	395 to 7.9

Checking of Interference of Foreign Ions and selectivity

Study of interference of different foreign ions in the new amperometric methods developed was carried out for three different concentrations of metal ions 5.0, 1.0 and 0.5 mM. The results have been summed up in Table-2. A large number of foreign ions were quite well tolerated. To avoid supersaturation, the maximum concentration of interfering species used was 0.25mol for the selectivity test.

Table 2: Tolerance Limit for Foreign Ions

Foreign Ions	Determination of Se(IV)	Determination of Se(VI)
$S_2O_3^{2-}$	1/20	1/20
Cl^-	A	A
NO_3^-	A	A
Ox_2^-	A	1
WO_4^{2-}	20 times	20 times
Mo(VI)	Equal	Equal
Mg(II)	A	A
Al(III)	Equal	Equal
V(V)	B	B
Cr(III)	1/20	1/20
Cr(VI)	B	B
Mn(VII)	B	B
Fe(III)	1/20	1/20
Co(II)	5 times	5 times
Ni(II)	Equal	Equal
Zn(II)	1/5	1/5
Cd(II)	1/20	1/20
Cu(II)	B	B
Tl(I)	Equal	Equal
As(III)	10 times	10 times
As(V)	A	A
CH_3COO^-	10 times	10 times
Se(IV)	-	1/20
Se(VI)	B	-

A- No interference even when concentration in cell solution is 20 times in excess to that of the metal ions in the titrant solution.

B - Serious interference even when foreign ion is 1/20 of metal concentration

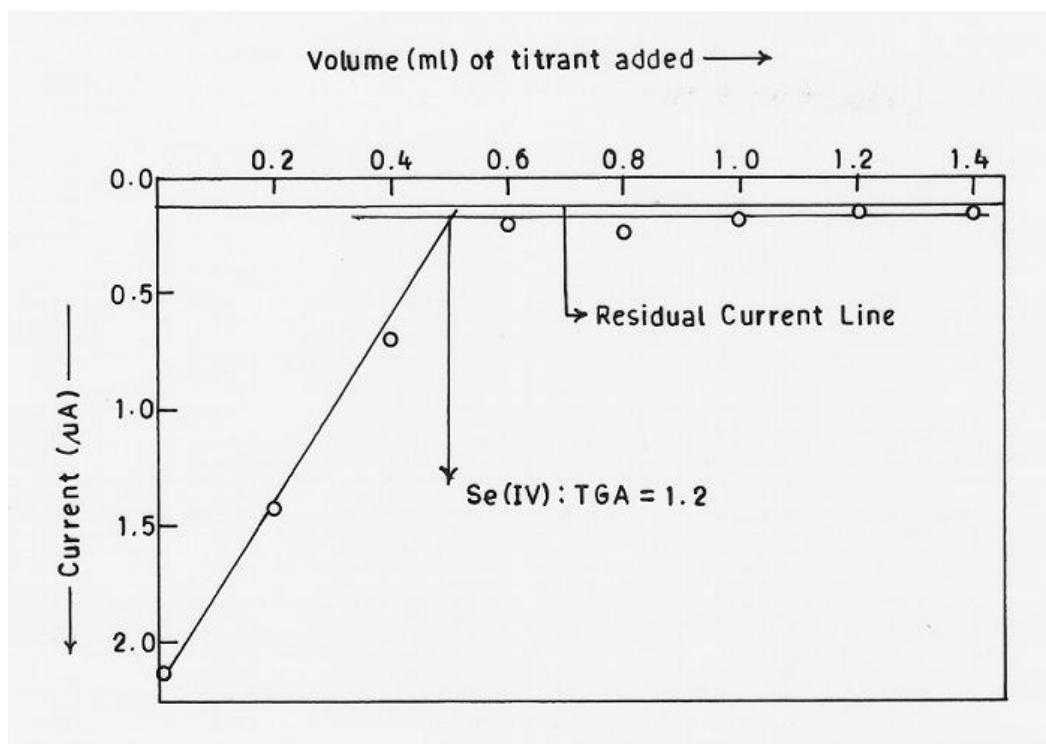


Figure 1: Amperometric titration curve of Se(IV)-TGA system in acetate buffer of pH 4.99 (anodic titration)

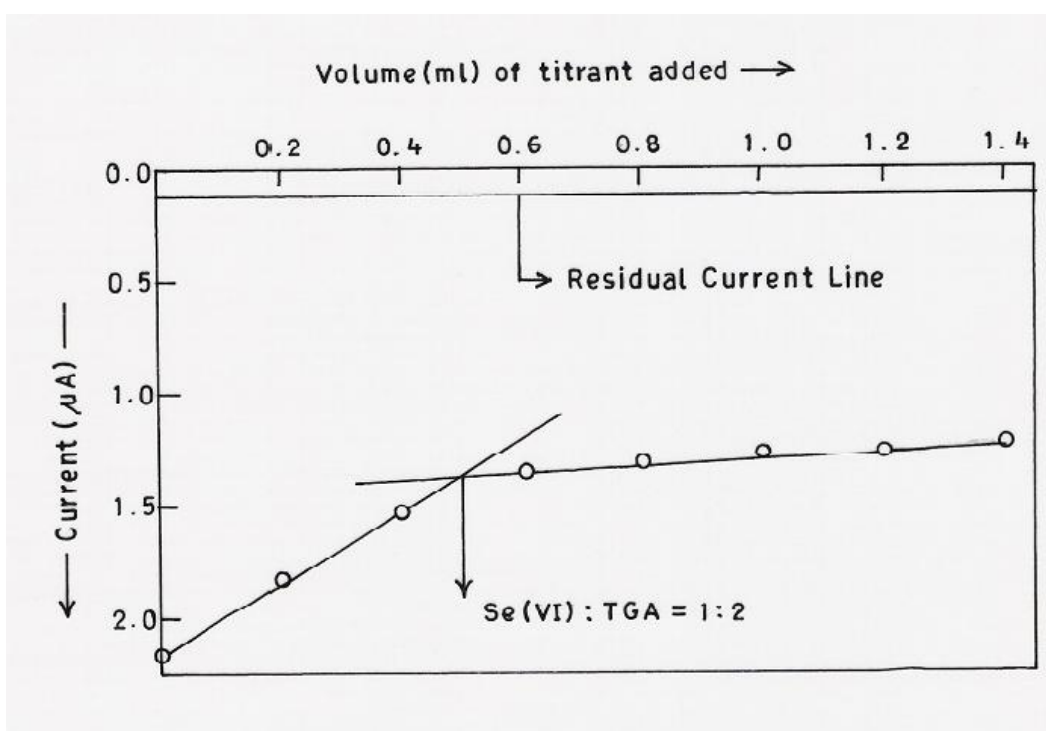


Figure 2: Amperometric titration curve of Se(VI)-TGA system in acetate buffer of pH 4.99(anodic titration).

CONCLUSION

The study shows that thioglycolic acid is suitable for the determination of trace quantities of Se(IV) and Se(VI). The Amperometric method gives reproducibility with standard deviation of 0.05 only. The technique has the added advantages for the developing

country like India in being relatively quick, economic and simple.

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