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TGA as an Amperometric Reagent for Trace Determination of Gold (III).

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ABSTRACT

In the present study, amperometric determination of Gold (III) was carried out. Thioglycolic acid (TGA) has been used for determination of Gold(III) at d.m.e. (dropping mercury electrode). 0.1M KCl and acetate buffer of pH 3.7 media have been employed as supporting electrolytes for the trace determination of Gold (III). Stoichiometry obtained for Gold (III)-TGA was 1:1 in both these media. The new amperometric method can be exploited for the estimation of Gold solution as dilute as 6.00ppm for cathodic titrations and 10.00ppm for anodic titrations successfully with high degree of accuracy in both these media. Maximum error ($\pm 2\%$) was encountered in case of most dilute solutions only. Studies of interference of foreign ions in the determination of Gold (III) were also investigated.

Keywords: Amperometric, Thioglycolic acid, Stoichiometry, Gold (III).

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INTRODUCTION

Gold (Au) is found in elemental or native form at the earth's surface. Cu(II), Ag(I) and Au(III) together, called the currency metals, since they have been used in coins since the beginning of money. Gold is one of the least reactive chemical elements, solid under standard conditions. It is one of the most valuable precious metals. Pure metallic (elemental) gold is non-toxic and non-irritating when ingested. The majority of gold is used as jewellery. It is also used in many food companies and in medicine. In this report gold(III) has been estimated using a sulphur containing organic ligand, thioglycolic acid abbreviated as TGA. Amperometric titration has also been used in past for trace determination of this metal with different ligands like Ethanethioic acid and 2- Mercapto and 3-Mercaptopropanoic acid [1, 2]. Many sulphur containing organic ligands have been used in amperometry for the trace determination of metal ions. Thioglycolic acid (TGA) formulated as HS-CH₂-COOH, has often been used as a complexing agent and analytical reagent [3-10]. This acid has also been used in grafted onto silica gel[11], in preparation and characterization of glass embedding [12], as potentiometric sensors [13] and in synthesizing nanorods and nanosheets [14]. This ligand have also been exploited earlier for the amperometric determination of some transition metals and non-metals [15,16]. The present work was undertaken with a view to extend the use of this ligand for the amperometric determination of Gold(III) in traces at d.m.e.

EXPERIMENTAL

The author used a Toshniwal (India) manual polarograph of the type CLO2A, in association with a polyflex galvanometer of type PL50 for recording polarograms as well as variation in current during amperometric titrations. Chloroauric acid, (HAuCl₄.xH₂O) was used as a source compound for Au(III). Stock solution of Au(III) [17] was standardized amperometrically. TGA solution was prepared fresh daily and standardized. Purified nitrogen gas was employed for deaeration. Amperometric determination of metal solution of any particular concentration was carried out at least thrice. Titration voltages were selected in the limiting region of cathodic wave of metal ions in case of cathodic titrations and limiting region of anodic wave of TGA in case of anodic titrations as TGA is also polarographically active. Cathodic titrations were performed with TGA solution as titrant at -1.00V. Anodic titrations were performed with Gold(III) solution as titrant at -0.10V. The selected potential was kept constant throughout the experiment. 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.

RESULT AND DISCUSSION

Amperometric determination of Au(III) was carried out in 0.1M KCl and acetate buffer of pH 3.7 media. Au(III) was observed by the author to give a well defined cathodic wave in this medium with its reduction current appearing from a potential more positive than 0.00V ($E_{1/2} >$

0.00V). A maximum appeared in the beginning of wave which, however, could be suppressed with 0.005% gelatin; a cleared limiting region appeared from -0.05V in presence of gelatin. But in acetate buffer of pH 3.7 medium the author observed a cathodic wave of Au(III) with limiting region starting from 0.00V ($E_{1/2} > 0.00V$), similar to one reported by Meites [18] in 2M acetic acid + 2M sodium (or ammonium) acetate medium. However, no maximum was observed in the medium used by the author at 0.1mM or lower concentrations of the metal species though the same did appear in the beginning of the limiting region at higher concentrations and gelatin had to be added to suppress it as reported (loc.cit.).

TGA was also polarographically active and it has been reported in past [19,20] to give a fully diffusion controlled, reversible and one electron anodic wave in 0.1M KCl and acetate buffer of pH 3.7 media with $E_{1/2}$ as -0.23V and -0.25V respectively. Similar wave was observed by the author with $E_{1/2} = -0.24V$ and -0.25V respectively in both the media.

Titrations of Au(III) with TGA solution were carried out at -1.00V and -0.10V for cathodic and anodic titrations, respectively. A cream colour emerged in the cell solution while titrating the metal species with TGA in 0.1M KCl medium and bluish colour in acetate buffer of pH 3.7. Stoichiometry of metal species: TGA was of 1:1 in both media. The titrations resulted in amperometric curves like Fig. 1 and Fig. 2 in 0.1 M KCl medium and like Fig. 3 and Fig. 4 in acetate buffer of pH 3.7 medium respectively.

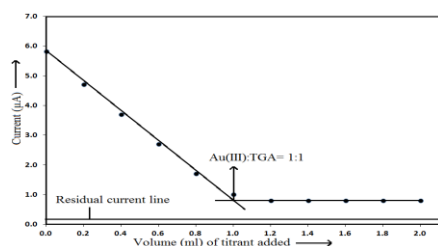


Fig 1: Amperometric titration curve of Au(III):TGA system in 0.1M KCl medium

Titration voltage : -1.00V
 Conc. of Au(III) : 0.50mM
 Conc. of in TGA thetitrant solution : 5.00mM

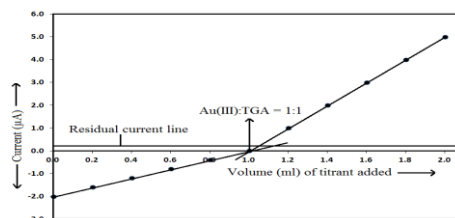


Fig 2: Amperometric titration curve of Au(III):TGA system in 0.1M KCl medium

Titration voltage : -0.10V
 Conc. of TGA : 0.50mM
 Conc. of in Au(III) thetitrant solution: 5.00mM

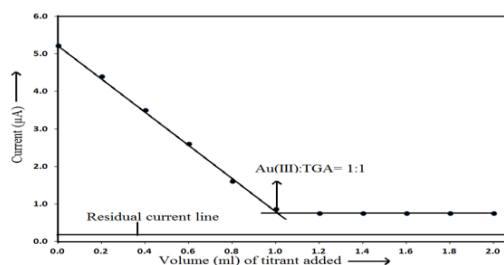


Fig 3: Amperometric titration curve of Au(III):TGA system in acetate buffer medium having pH 3.7

Titration voltage : -1.00V
 Conc. of Au(III) : 0.50mM
 Conc. of in TGA the titrant solution : 5.00mM

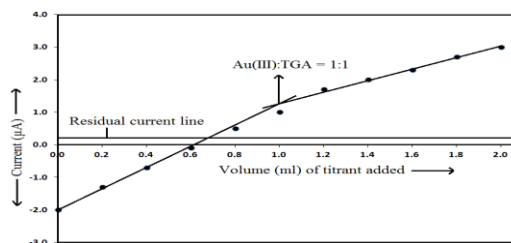


Fig 4: Amperometric titration curve of Au(III):TGA system in acetate buffer medium having pH 3.7

Titration voltage : -0.10V
 Conc. of TGA : 0.50mM
 Conc. of in Au(III) the titrant solution : 5.00mM

Probability of complex formation (involving Au(III) and TGA) being the fundamental basis for the titrimetric method developed seems to be maximum. The wave pertained to three electron reduction of Au(III) at d.m.e. as suggested by earlier workers [17,21] in media similar to those employed by the author. Any redox reaction can be safely ruled out in view of the 1:1 stoichiometry obtained, as the organic acid (TGA) normally provide one-electron for reduction, giving ultimately a product like MPS-SMP [22] and Au(III) required two-electrons to be reduced to Au(I), Au(II) state being non-existent [23]. Besides, a cream colour emerged in the cell solution while titrating the metal species with TGA in 0.1M KCl medium and bluish colour in acetate buffer of pH 3.7; this may be indicative of complex formation between Au(III) and TGA. It is noteworthy that Schoeller and Allardt [24] and Rajesh Malik [25] had observed the emergence of cream colour (light yellow) on reacting with similar organic ligand (2-mercapropoanoic acid, having one -SH and one -COOH group and also dark blue colour [25] with 3-mercapropoanoic acid) with Au(III) and suspected complex formation. Rajesh malik [25] had also reported the 1:1 titrimetric molar ratio in case of cathodic titrations.

Au(III) being a soft species, is expected to have a strong affinity for the soft sulphur donor atom of the ligand. In fact, TGA can very well act as bidentate ones, coordinating through

mercaptide and carboxylate /carbonyl groups. However, nothing can be said with certainty about the exact nature of the complex likely to be formed during titrations.

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	Au(III)		Au(III)	
	0.1M KCl		Acetate buffer of pH 3.7	
Foreign ion	Cathodic titration	Anodic titration	Cathodic titration	Anodic titration
Cl ⁻	B	B	B	B
NO ₃ ⁻	B	B	B	B
CH ₃ COO ⁻	B	B	B	B
Ox ²⁻	B	B	B	B
WO ₄ ²⁻	1/5 th	Equal	1/5 th	10t
Mg(II)	B	B	B	B
Al(III)	B	B	B	B
V(V)	A	A	10t	5t
Cr(III)	A	A	B	B
Cr(VI)	1/10 th	1/10 th	A	A
Mn (II)	B	B	B	B
Mn (VII)	1/5 th	1/10 th	A	1/10 th
Fe(II)	A	A	Equal	Equal
Fe(III)	A	A	B	B
Co(II)	Equal	Equal	5t	Equal
Ni(II)	B	B	Equal	10t
Cu(II)	1/5 th	Equal	Equal	1/10 th
Zn(II)	B	B	B	B
Mo(VI)	A	A	1/5 th	10t
Cd(II)	Equal	B	1/10 th	1/5 th
Hg(II)	A	A	1/5 th	1/5 th
As(III)	1/10 th	5t	5t	5t
SO ₄ ²⁻	B	10t	B	B
SCN ⁻	B	B	1/20	B
Os(VIII)	A	1/10 th	1/5 th	1/10 th
Ag(I)	A	A	1/5 th	1/10 th
Pt(IV)	A	A	A	A
Rh(III)	1/10 th	1/5 th	1/10 th	1/5 th
Pd(II)	1/10 th	1/20 th	Equal	A
Ir(III)	1/5 th	5t	1/10 th	1/5 th
Ru(III)	Equal	5t	1/10 th	Equal

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

t = times

Study of amperometric titrations reveals that cathodic titrations are more sensitive in comparison to anodic ones and also superior to the old amperometric methods [25] being encountered comparatively low error in titrating dilute solutions. Even these, however, are not

as sensitive as common spectrophotometric methods listed by Meites [26] and also have low degree of tolerance for other coinage and platinum metal ions. Still this amperometric method beat these methods in being valid over a wider range of concentrations and being economic, amperometric process is more considerable.

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.

CONCLUSIONS

The study shows that thioglycolic acid is suitable for the determination of trace quantities of Au(III). 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, economic and simple.

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