

NEW AMPEROMETRIC METHODS FOR THE TRACE DETERMINATION OF Rh(III) AND Ir(III)

Ritu Langyan, Dayawati and SP. Khatkar*

Department of Chemistry, M.D. University, Rohtak, Haryana, India.

ABSTRACT

Amperometric determination of Rh(III) and Ir(III) was successfully carried out with the help of thioglycolic acid (TGA) at dropping mercury electrode (d.m.e.). 0.1M NH₃ + 0.1M NH₄Cl medium has been employed for Rh(III) and 0.1M NaClO₄ medium for Ir(III). Only anodic titrations were carried out successfully for Rh(III) and only cathodic titrations were carried out in case of Ir(III). Metal species-TGA stoichiometry obtained was 1:2 for both the metal ions in respective mediums. Solutions as dilute as 5.15ppm (Rh) and 9.61ppm (Ir) were estimated with high degree of accuracy by these new amperometric methods. Tolerance limit for foreign ions has also been worked out.

Keywords: Amperometric determination, Thioglycolic acid, Rh(III) and Ir(III).

INTRODUCTION

There are various techniques for estimation of these metals out of them amperometry is one of economic technique. Amperometric titration has also been used in past for trace determination of these metals with different ligands like ethanethioic acid and 2-mercapto and 3-mercapto propanoic 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 reagent³⁻¹⁰. This acid has also been used in grafted onto silica gel¹¹, in preparation and characterization of glass embedding¹², as potentiometric sensors¹³ and in synthesizing nanorods and nanosheets¹⁴. This ligand has also been exploited earlier for the amperometric determination of coinage metals, some transition metals and non-metals¹⁵⁻¹⁷. The present work was undertaken with a view to extend the use of this ligand for the amperometric determination of Rh(III) and Ir(III) in traces at d.m.e.

EXPERIMENTAL

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. Iridium chloride (IrCl₃) and rhodium chloride (RhCl₃.xH₂O) were used as a source compounds for Ir(III) and Rh(III) respectively. TGA solution was prepared fresh daily. Rh(III) solution was standardized by amperometric method¹⁸ while Ir(III) was prepared by weighing. Amperometric determination of metal solution of any particular concentration was carried out at least thrice. Purified nitrogen gas was employed for deaeration. The potential selected for titrations was kept constant throughout. 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

Determination of Rh(III)

Amperometric determination of Rh(III) was carried out in 0.1M NH₃+0.1M NH₄Cl supporting electrolyte. Rh(III) was observed by the author to give a well defined cathodic wave in this medium with its limiting region spread

over a small potential region from -0.40V through -0.60V with $E_{1/2} = -0.24V$. Titration of Rh(III) with the TGA solution (cathodic titration) was carried out at -0.40V. Complexation of Rh(III) with thiomalic acid, 2-mercapto and 3-mercaptopropanoic acid has been reported^{18,19}. This voltage fell in the limiting region of cathodic wave Rh(III) and TGA both. The titration resulted in amperometric curve shown in Fig-1. The null point corresponded to the metal species:TGA molar reaction ratio of 1:2. The method enabled the estimation of Rh(III) solution in the concentration range of 514.53ppm through 5.15ppm. Maximum error ($\pm 2\%$) was encountered in the case of most dilute solution only. This new amperometric method is quite efficient. Results were also supported by previous studies of our laboratory.

Determination of Ir(III)

Ir(III) was reported to give a well-defined, irreversible, cathodic wave in 0.1M NaClO₄ medium with the short limiting region stretching from -1.10V through -1.30V with half wave potential ($E_{1/2}$) = -0.96V. Similar wave was observed by the author in her medium, 0.1M NaClO₄ medium, with $E_{1/2} = -0.86V$. Titrations of Ir(III) with the TGA solution (cathodic titrations) were carried out at -1.10V.

Complexation of Ir(III) with 2-mercapto and 3-mercaptopropanoic acid has been reported. This voltage fell in the limiting region of Ir(III) alone; no anodic current of TGA was present here. The titration resulted in amperometric curve shown in Fig-2. The null point corresponded to the metal species:TGA molar reaction ratio of 1:1. The method enabled the estimation of Ir(III) solution in the concentration range of 961.10ppm through 9.61ppm. Maximum error ($\pm 2\%$) was encountered in the case of most dilute solution only. This new amperometric method is quite efficient. Results were also supported by previous studies of our laboratory.

CHECKING OF INTERFERENCE OF FOREIGN IONS AND SELECTIVITY

Study of interference of foreign ions in the new amperometric methods was carried out for three concentrations of each metal species viz 5.00mM, 1.00mM and 0.50mM. 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 0.25mM 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 | Rh(III) | Ir(III) |
|----------------------------------|--|-------------------------|
| Medium | 0.1M NH ₃ + 0.1M NH ₄ Cl | 0.1M NaClO ₄ |
| Foreign ions | Cathodic titration | Cathodic titration |
| Cl ⁻ | B | B |
| NO ₃ ⁻ | B | B |
| CH ₃ COO ⁻ | B | B |
| Ox ²⁻ | B | B |
| WO ₄ ²⁻ | B | B |
| Mg(II) | B | B |
| Al(III) | B | B |
| V(V) | 5t | 5t |
| Cr(III) | B | B |
| Cr(VI) | 1/5 | 1/5 |
| Mn (II) | B | B |
| Mn (VII) | 1/10 | 1/5 |
| Fe(II) | Equal | 5t |
| Fe(III) | 1/5 | A |
| Co(II) | Equal | equal |
| Ni(II) | A | A |
| Cu(II) | A | Equal |

| | | |
|------------------|------|-------|
| Zn(II) | A | 1/10 |
| Mo(VI) | 1/10 | Equal |
| Cd(II) | 1/5 | 5t |
| Hg(II) | 1/5 | A |
| Au(III) | A | A |
| As(III) | A | 1/10 |
| SCN ⁻ | B | B |
| Pd(II) | A | 10t |

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

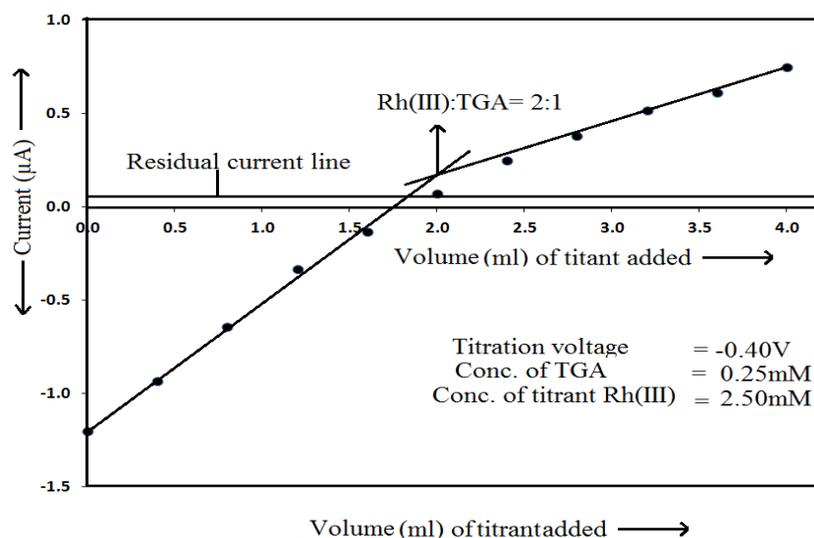


Fig. 1: Amperometric titration curve of Rh(III):TGA system in 0.1M NH₃ + 0.1M NH₄Cl medium

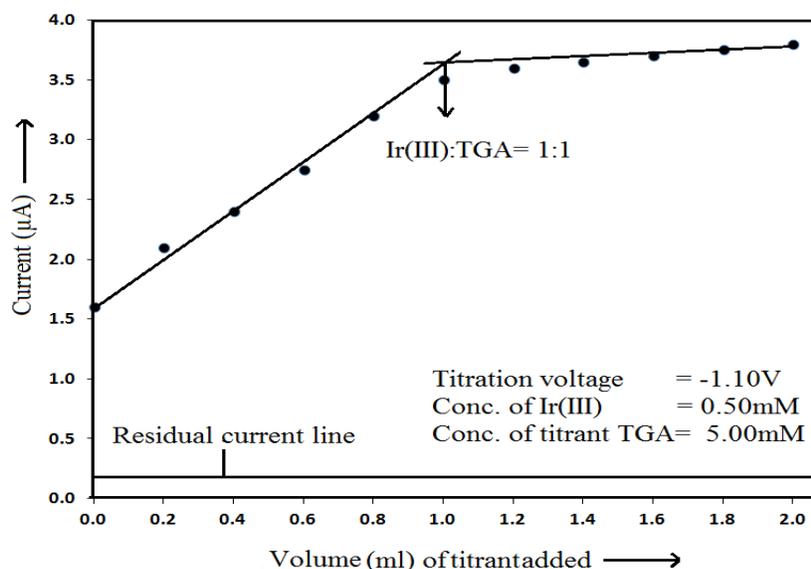


Fig. 2: Amperometric titration curve of Ir(III):TGA system in 0.1M NaClO₄ medium

CONCLUSIONS

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

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