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# Determination of Ru (III) Metal-ions in Solution at Trace Level by Ethanethioic Acid (ETA) as Ligand by Amperometric Method

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***Abstract:***

*This new method of trace analysis Ru(III) metal ions by amperometric titrations with the help of organic ligand ethanethiol acid (ETA) by using dropping mercury electrode (d.m.e) Vs S.C.E is reported in the new medium consisting of supporting electrolyte 2.0 M RbCl in 7% acetic acid. The cathodic reduction of Ru (III) occurs in two stages in this medium and has been reported in the literature. The organo-sulfur ligand ETA was also found to give its characteristic reversible, one-electron anodic wave with a Half-Wave Potential of -0.174V. The ligand ETA is used as a titrant in the amperometric titrations, carried out only at some constant voltage (here,- 0.05 V) which falls in the common limiting region of the ligand ETA as well as 1st cathodic wave of metal ions of Ru (III). Though, no indication of chemical reaction was observed between these two species not indicated, the basis of this new titrimetric method seems to be the current compensation phenomenon (the beauty of amperometric). Ru (III): ETA null point molar ratio is 1:0.66 and Ru (III) solutions up to 4 ppm can be estimated with a fair degree of accuracy. The study of various interfering cations and anions is also reported in this new method.*

***Keywords**:*

*Amperometry, Ethanethioic acid, Ruthenium, d.m.e., current compensation.*

## Introduction

Right from the beginning of civilization, chemists have a great interest in the analysis of metal ions at trace levels. Many methods of estimation up to trace analysis of the transition metal ions solution have been reported in literature like Polarography, Voltammetry, Amperometry etc. This new amperometric method was developed for the trace determination of Ru (III) metal ions with ethanethioic acid (ETA) and was carried out in a medium consisting of 2.3M RbCl in 7% acetic acid (pH = 2.45).

## Determination of Ru (III) with ETA:

This new amperometric determination of the metal species with ETA was carried out in a medium consisting of 2.3M RbCl supporting electrolyte in 7% acetic acid (pH=2.45) employing the organic-sulfur compound as titrant in cathodic titrations. The molar ratio of metal species-ETA was found 1:0.66 at the null point. These titrations are solely based up on the phenomenon of current compensation and carried out only at the voltage in the common limiting region of both the species i.e. metal ion & Ligand. Amperometric determination of the metal species with MPSH has already been reported by O.P. Agrawal and S.P. Khatkar[282] in this medium. Any other medium may also be suitable for this titration.

## Polarographic Characteristics of the Metal-ion

The Polarography can be used to study Ru (III) metal ions by observing their reduction to Ru (II) at a dropping mercury electrode. The reduction process can be quasi-reversible, meaning that the rate of the electrode reaction is not as fast as a fully reversible reaction. The diffusion currents observed during the reduction are proportional to the height of the mercury reservoir. Additionally, the half-wave potential (E1/2 = -0.15) and the slope of the <u>log id/I vs Ered~</u> plot can provide information about the reversibility of the reduction process and the and there is no complexation between the Ru (III) metal ion and organic species ETA.

## Polarographic Characteristics of ETA:

ETA was observed by the author to give its characteristic reversible, one-electron anodic wave in this medium with the short limiting region spread over the potential range of 0.00V through -0.7V. The polarogram did not show any pre-wave[396]. The value of E3/4-E1/4, [(- 0.150V) - (-0.205V)], was found to be 0.055V, E1/2 being -0.175V. Diffusion control of the wave and proportionality of its height to the concentration of ETA in the cell was checked and found to be good.

**Table 1.1**

**Checking of diffusion control of ETA (0.50mM) wave in the medium consisting of 2.3M RbCl in 7% acetic acid**

| Height (h) of the mercury column (cm.) | i1 (□a) at -0.05V (residual current excluded) | i1⍁ h |
|---|---|---|
| 30 | 0.628 | 0.1141 |
| 40 | 0.710 | 0.1121 |
| 50 | 0.798 | 0.1120 |
| 60 | 0.889 | 0.1136 |

**Table 1.2**

**Checking of proportionality of the diffusion current of ETA to its concentration in the medium consisting of 2.3M RbCl in 7% acetic acid; h = 40 cm**

| Conc. (c) of Ru(III) (mM) | id at -0.05V□(a) | id/c |
|---|---|---|
| 5.000 | 7.124 | 1.424 |
| 1.000 | 1.435 | 1.432 |
| 0.500 | 0.712 | 1.419 |
| 0.250 | 0.362 | 1.435 |
| 0.70 | 0.146 | 1.434 |

Average id/c at -0.05V = 1.432

**Amperometric Titrations Study:**

The first wave of Ru (III) was exploited for the amperometric determination at -0.05V, which fell in the diffusion region of both the metal species and organic sulfur compound. On titrating the Ru (III) solution with ETA, the cathodic current was progressively compensated by the anodic current of the acid. The titration curve reached the null point (i.e. intersected the residual current line) when the molar concentration ratio of Ru (III) and ETA was 1:0.66. The addition of more ETA led to the appearance of an anodic current with a slight change in the slope of the curve. No color change occurred in the course of titrations. The results of titrations are given in Table 1.1.

**Table 1.3**

**Amperometric determination of Ru (III) with ETA in the medium consisting of 2.3M RbCl in 7% acetic acid**

| Titrant | : | ETA |
|---|---|---|
| Titration Voltage | : | -0.05V |
| Range of Conc. of ETA used | : | 50.00mM-0.50mM |

| Conc. of Ru (III) taken ppm | Conc. of Ru (III) obtained (Mean) ppm | %age error (Mean) | Standard deviation |
|---|---|---|---|
| 505.35 | 505.35 | 0.00 | 0.00 |
| 71.07 | 71.07 | 0.00 | 0.00 |
| 50.54 | 50.54 | 0.00 | 0.00 |
| 25.27 | 25.27 | 0.00 | 0.00 |
| 7.11 | 7.01 | 0.99 | 0.30 |
| 5.05 | 4.92 | 2.37 | 0.33 |
| 2.33 | 2.40 | 5.13 | - |

Titration at -0.40V, (2nd wave region of $Ru^{II}$) where the ETA wave was totally absent, brought about no reduction in the cathodic current. This discounted any possibility of chemical interaction between the two species. That the basis of the titration is only the phenomenon of current compensation is indicated by the nature of the amperometric curve as well as the fact that the titrimetric Ru (III): ETA ratio (1:0,66) for the id/c of ($Ru^{III}$-1st wave). It is noteworthy that the average id/c of Ru (III) is 1.615 while that of ETA is 1.432. The reverse titration, using Ru (III) as titrant, was also performed at -0.05V. Anodic current of ETA decreased with the advancing titration, finally yielding to the emergence and linear increase of the cathodic current. However, the Ru (III)-ETA ratio at the point of intersection of the residual current line was found to be different for different concentrations of metal species. This form of titration, consequently, cannot be recommended.

Interestingly, the new method did not yield good results if the concentration of RbCl in the medium was kept lower. Thus, the titration of the metal ion solution with ETA in a medium consisting of 0.1M RbCl or 1.0M RbCl in 7% acetic acid, failed because no fixed titrimetric M- ETA ratio could be obtained. Similarly, any concentration of RbCl without acetic acid was also not found suitable.

**Checking of Interference and Selectivity**

The interference of various cations and anions in the cathodic titrations was checked. Three concentrations of Ru (III), viz. 505.35 ppm, 71.07 ppm and 5054 ppm were selected for such studies. Mg(II), WO42-, SO42-, $Ox^{2-}$ and $Cl^-$ did not interfere in these titrations even when present in the cell solution in concentrations 15 times in excess of that of Ru(III) in that solution while Mn(I), Mn(VIII), Fe(II), Fe(III), Co(II), Cu(II), Rh(III), Pd(II), Cd(II), Os(VIII), Ir(III), Pt(IV), Au(III), Pb(II), MoO42- and S2O32- interfered seriously at all concentrations. Safe limit of other foreign ions in the cell solution, has been included in the tavle-1.4.

The non-interfering foreign ions did not interfere even when added to the cell solution simultaneously. An equal concentration of all the non-interfering ions was maintained in the cell for these selectivity tests, the maximum being 0.25mM. Higher concentrations were not attempted in order to avoid the supersaturation of the solution in the cell. Ru (III) concentrations selected for this study were the same as mentioned above in the case of interference studies.

**Table 1.4**

**The safe limit of the concentration of foreign ions in the cell solution with respect to the concentration of the metal species determined with ETA**

| Foreignion | Relative safe limit | Foreign ion | Relative safe limit |
|---|---|---|---|
| Al(III) | 15 | Ni(II) | 7 |
| V(V) | 1/20 | Zn(II) | 15 |
| Cr(III) | Equal | $NO3^-$ | 1/7 |

**Note:** *Table 1.5 shows that even a 2.33 ppm solution of Ru (III) can be quite accurately estimated with ETA, mean %age error encountered being less than ±5.*

**Discussion**

Amperometric determination of Ru (III) with the help of ETA was perfected in the medium consisting of 2.3M RbCl solution in 7% acetic acid. The exact composition of this supporting electrolyte medium was established by trial-and-error method. The new methods required the use of organic acids as titrants. A method with MPSH is already available in the literature[282] and the author could not carry out any improvement over the same.

The polarographic activity of both ETA in the medium was observed by the author. The organic acid ETA gave their usual one-electron anodic wave with short diffusion regions spread over the potential range of -0.02V for ETA.

Ru (III) gave two reduction waves in this medium.[281] The 1st wave started at a potential more positive than 0.00V and E1/2 and the number of electrons involved in the electrode reaction could not be checked. The diffusion region of this wave stretched over the potential range of -0.04 through -0.20V while that of the 2nd wave stretched from -0.30V through -0.60V. The 2nd wave was rather ill-defined and its E1/2 also could not be ascertained[281]. The first wave was fully diffusion controlled while the 2nd wave was not. The proportionality of the height of the 1st wave to Ru (III) concentration in the cell was rechecked by the author (Table-1.2) and found good, while, as reported (loc.cit) it was not so in the case of the 2nd wave. O.P. Agrawal and S.P. Khatkar[49] have proposed the following electrode reaction for the two waves:

It seems the new amperometric methods like the MPSH method reported[282] do not entail any chemical interaction and are based solely on the phenomenon of compensation of the cathodic current of the 1st wave of Ru (III) by the anodic current of the organic sulfur compounds. It may be mentioned that the titration voltage (-0.05V) fell in the diffusion regions of both the species (metal and the organic acid) and no suppression of the cathodic current of Ru (III) occurred if any of the organic acid (ETA or ETA) was progressively added at a voltage (e.g. - 0.40V, which lay in the region of 2nd wave of $Ru^{III}$) where the anodic current was totally absent.

It is also noteworthy that the Ru (III)-organic acid titrimetric ratio of 1:0.66 (ETA) is equal to the reverse of the ratio of id/c of the two species; the average id/c for Ru (III) is 1.601 and that of ETA was 1.423. The nature of the amperometric curves (almost straight line with only a slight change of slope at the null point which falls right on the residual current line also indicates the operation of the current compensation phenomenon[281,500,501.]

## Conclusion

The new methods enable the estimation of Ru (III) solutions as dilute as 5.05 ppm with great accuracy. Even 2.33 ppm solutions could be estimated with ETA reasonably accurately with the maximum error encountered being in the neighborhood of 5%. In this matter, these methods prove to be somewhat superior to the two older methods available in the literature[281,282]. All these (old and new methods) show a very low degree of tolerance for coinage and platinum metal ions. In this new method, interference of other foreign ions is lesser and the accuracy of determination of most dilute solutions slightly better in the case of ETA methods. This method is valid for a far greater range of concentrations of Ru (III) solutions in comparison to common spectrophotometric methods of determination[502].