

CHAPTER-IV



AMPEROMETRIC ESTIMATION OF SOME TRANSITION METALS AND RARE EARTHS

Introduction

It has been shown in the chapter No. 2, that the limiting current is independent of the applied voltage impressed upon a dropping mercury electrode. The only factor affecting the limiting current, if the migration current is almost eliminated by the addition of sufficient supporting electrolyte, is rate of diffusion of electro active material from the bulk of the solution to the electrode surface.

Hence the diffusion current (limiting current- residual current) is proportional to the concentration of electroactive material in the solution. If some of the electroactive material is removed by interection with a reagent, the diffusion current will decrease. This is fundamental principle of amperometric titration.

The observed diffusion current at a suitable applied voltage is measured as a function of the volume of the titrating solution.

The end point is the point of intersection of two lines giving the change of current before and after the equivalence point. In amperometric titrations the current which passes through the titration cell between an indicator electrode and reference electrode (e.g. the saturated calomel electrode) at a suitable applied emf is measured as a function of the volume of the titrating solution. These titrations are advantageous over conventional potentiometric and conductometric titrations as regards to the accuracy and precision of the results.

Survey of Literature

A survey of literature reveals that the first amperometric titration was performed by Heyrovsky and Berezicky. Since then the technique has been employed successfully to estimate various cations and anions. However, very few references are available on the amperometric estimation of rare earths.

Misumi and Iswase¹ estimated rare earths, amperometrically, with DTPA and reported 1:1 chelate formation in each case. Pitre and Lavale² determined La, Ce, Pr, Nd with cupferron in hydrochloric acid medium at pH 2.75 ± 0.02 at an applied potential -1.2 V vs SCE on the cupferron wave using a DME. Stoichiometry of the complexes was found to be 1:1.

Rolthoff and Jacobson³ have performed the permanganate titration of Ce(III) ion in 0.25 mol dm^{-3} in pyrophosphate buffers at pH 5 and 8 at a rotating platinum electrode at zero potential.

In our laboratory, Pitre and Lavale⁴ have reported the amperometric estimations of some lanthanides with ARS, PAR, PAN and Xylenol orange⁴.

Pitre and Chitle⁵ have reported amperometric estimation of tatrazine and naphthaline scarlet 4RS with trivalent La, Ce, Pr and Nd. Spectral studies on complexes of rare earth metal ions with PAN and PAR have been done by Rao and Raddy⁶.

The present chapter deals with amperometric estimations of Zr^{4+} , Tb^{3+} , Dy^{3+} , Er^{3+} and Sm^{3+} ions with PAN, PAR, methylene blue and 1, 10 phenanthroline.

Experimental

All the chemicals used were of Anal R/BDH grade, stock solutions of 1-2 (Pyridyl azo) 2-Naphthol, 4-2 (Pyridyl azo) Resorcinol, methylene blue and 1, 10, Phenanthroline ($0.01 \text{ mole/dm}^{-3}$) were prepared by direct weighing the requisite quantity of the chemicals and dissolving it in doubly distilled water and (20:80) water : ethanol solvent. Erbium (III) nitrate, Sm(III) nitrate and Zr(IV) nitrate (Riedel, Hungary) solution ($0.01 \text{ mole dm}^{-3}$) was also prepared by dissolving the requisite quantity of chemicals in doubly distilled water and solution was standardised⁷. The solutions of Dy(III) and Tb(III) ($0.01 \text{ mole dm}^{-3}$) were prepared by heating requisite quantity of their oxides in concentrated HCl to dryness and residue was extracted in doubly distilled water. 1 mol dm^{-3} KCl and 0.01% gelatin solutions were prepared in double distilled water and hot distilled water respectively.

Ionic strength of 0.1 mol dm^{-3} was adjusted with KCl and dilute HCl and NaOH were used to adjust the pH at 3.10 ± 0.1 .

Polarographic behaviour of the titled metal ions (rare earths) and the analytical reagents PAN, PAR, methylene blue and 1, 10, phenanthroline were studied in 0.1 mol dm^{-3} KCl + 0.001% gelatin at

pH=3.1±0.1. It was observed that the metal ions produce polarographic signal only after applying voltage, higher than -1.70 V *vs* SCE. Whereas, the aforesaid analytical reagents produced well defined polarographic waves. The diffusion current for each polarogram was found to be proportional to the concentration of the reagent. The plateau potentials on the polarographic waves of each reagents viz. PAR = -0.85V, PAN = -0.60V, MB = -0.40V and 1, 10 phenanthroline = -1.42 V *vs* SCE were fixed for amperometric titrations. At these potentials the rare earths under study do not produce any polarographic signal.

Amperometric titrations were made on a manually operated polarograph equipped with multiflex galvanometer (sensitivity 8.10×10^9 amp/div) using dme as an indicator electrode and Saturated Calomel Electrode (SCE) as reference electrode. The capillary used had a *m* value of 2.15 mg/sec and drop time of 3.1 sec. at 45cm effective height of mercury column. Dissolved oxygen was removed by passing purified nitrogen gas through the test solution for about fifteen minutes before the titrations. Systronics (India) pH meter model LI-335 was used for pH measurements.

Results and Discussion

Amperometric determination of Zr(IV), Tb(III), Dy(III), Er(III) and Sm(III) ions with 1-2 (Pyridyl azo) 2-Naphthol :

Trace estimations of titled rare earths have been carried out with an important azo metalo chromic indicator, PAN.

For titrations, sets of solutions containing a known amount each of Zr(IV), Tb(III), Dy(III), Er(III) and Sm(III) in 0.1 mol dm^{-3} KCl and 0.001% gelatin were prepared separately. The pH of these solutions was adjusted with dilute HCl-NaOH to 3.10 ± 0.1 . The test solution was taken in titration cell. The plateau potential of PAN in 0.1 mole dm^{-3} KCl was applied on the potentiometer (at which Zr(IV), Tb(III), Dy(III), Er(III) and Sm(III) ions are unattacked) and the current was noted on the galvanometer. The solution of PAN was then added drop by drop from a 1 cm^3 semimicro burette. Red colouration was observed. The current was noted after each addition of PAN. On plotting galvanometer reading after necessary volume correction against titrant volume a reversed L shaped curve was obtained (Fig. 4.1, 4.2, 4.3 and 4.4). The end point revealed a metal to PAN ratio of 1:1. Although, Munshi and Dey⁸ have reported 1:3, metal : PAN ratio, on the basis of spectrophotometric observations, but this discrepancy in the observed and literature value may be explained on the basis of the lower experimental pH and lower concentration of PAN used by the author. The data presented in table 4.1, 4.2, 4.3 4.4 and 4.5

clearly indicate that this method can be successfully applied for the estimation of trace amounts of the titled metal ions, with an error less than 1 percent.

Interference studies :

Effect of diverse ions on the amperometric titration procedure was studied by adding a known amount of foreign ions to the test solution and performing the titration in the earlier discussed way. Alkali and alkaline earth metal ions, NH_4^+ , Cl^- , ClO_4^- , NO_3^- , SO_4^{2-} and CH_3COO^- do not hamper the titration procedure, whereas a small amount of Cd^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Bi^{3+} and rare earths interfered the titration procedure seriously.

Amperometric determination of Zr^{4+} , Tb^{3+} , Dy^{3+} , Er^{3+} and Sm^{3+} with 4-2 (Pyridyl azo) resorcinol :

This azo dye also forms brilliant Scarlet red lakes with all the titled metal ions at the higher pHs. However, it changes to yellow orange as pH of the solution decrease.

For amperometric titrations sets of solutions containing a known amount of each of the rare earth in 0.1 mol dm^{-3} potassium chloride and 0.001% gelatin separately. The pH of the solutions was adjusted to 3.1 ± 0.1 with HCl/NaOH solution. The amperometric titrations were performed at the plateau potential of PAR i.e., -0.80 V vs SCE at which the titled metals do not produce polarographic wave. Current readings, noted after each addition of the titrant, when

plotted against volume of titrant, a reversed L shaped curve was obtained (fig. 4.1, 4.2, 4.3, 4.4). The end point indicated metal to PAR ratio to be 1:1. It may be mentioned here that the literature records metal : PAR ratio of 1:2. The difference between the authors observations on the basis of amperometric titration and the literature value may be explained on the basis of the changed experimental conditions used by the author i.e., lower pH and very low concentration of the ligand (PAR).

The data presented in table 4.6, 4.7, 4.8, 4.9 and 4.10 clearly indicate that this method can be successfully applied for the estimation of trace amount of the titled metal ions, with an error of less than 1%.

Interference studies :

Effect of diverse ions on the amperometric titration procedure was studied by adding a known amount of foreign ion to the test solution and performing the titration in the earlier discussed way. Alkali and alkaline earth metal ions NH_4^+ , Tl^+ , Cl^- , ClO_4^- , NO_3^- , SO_4^{2-} and CH_3COO^- do not hamper the titration procedure, whereas a small amount of Cd^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Bi^{3+} and rare earths interfered the titration procedure seriously.

The data presented in table 4.6, 4.7, 4.8, 4.9 and 4.10 clearly indicate that this method can be successfully applied for the

estimation of trace amount of the titled metal ions, with an error of less than 1%.

Amperometric determination of Zr^{4+} , Tb^{3+} , Dy^{3+} , Er^{3+} and Sm^{3+} with methylene blue :

Methylene blue is an adsorbable dye of thiazine group. It gives a well defined reduction wave in BR buffer with $E_{1/2} - 0.02$ V *vs* SCE at pH 2.9 and with $E_{1/2}$ value of -0.19 V *vs* SCE at pH 4.9¹⁰.

After fixing the desired plateau potential -0.4 V *vs* SCE the amperometric titrations were performed by adding a standard solution of methylene blue drop by drop from a semi micro burette (1.0 cm³) and the current was noted. The solution turns initially blue which gets precipitated on standing for long time. On plotting the galvanometer reading after necessary volume corrections against titrant volume, reversed L shaped curve (fig. 4.1, 4.2, 4.3 and 4.4) was obtained.

The end point indicated a metal to methylene blue ratio of 1:1. The data depicted in table 4.11, 4.12, 4.13, 4.14, 4.15 clearly indicate that this method can be successfully employed for the trace estimations of Zr^{4+} and trivalent Tb, Dy, Er and Sm, with an error of less than 1%. The accuracy and precision of the method has also been reported in the table.

Study of effect of diverse ions :

It was observed that some trivalent metals like Fe^{3+} and In^{3+} and transition metals like Pb^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} and rare earth badly affect the proposed amperometric estimation procedure. Ions like PO_4^{3-} , SO_4^{2-} , NO_3^- , Cl^- , I^- , ClO_4^- and CH_3COO^- do not interfere the said procedure even if present in fifty fold excess to the metal ion under estimation.

Under optimum conditions as described above, methylene blue has proved to be a selective reagent to detect the trace quantities of rare earths as low as 1.6 mg of each ions with the experimental error below 1% in each case. The statistical data also support the above view.

Amperometric determination of Tb(III), Dy(III), Er(III) and Sm(III) with 1, 10 phenanthroline :

1,10, phenanthroline is most widely used as a reagent for volumetric and spectrophotometric estimation of Iron¹¹. It shows a colourless to light blue colour change with pH which may find its use as a metallochromic indicator. However, no attempt seems to have been made to its use as a metallochromic indicator in estimation of rare earths and transition metals, amperometrically.

After fixing the desired plateau potential - 1.42 V *vs* SCE, the amperometric titrations were performed by adding a standard solution of 1, 10 phenanthroline drop by drop from a semi micro burette

(1.0 cm³) and the current was noted. On plotting the galvanometer reading after necessary volume corrections against titrant volume, a reversed L shaped curve was obtained. The end point indicated metal to 1, 10 phenanthroline ratio of 1:1. The data depicted in the table 4.16, 4.17, 4.18, 4.19 and 4.20 clearly indicate that this method can be successfully employed for the trace determination of Zr⁴⁺, Tb³⁺, Dy³⁺, Er³⁺ and Sm³⁺ with an error of less than 1%. The accuracy and precision of the metal has also been reported in the table.

Study of the effect of diverse ions :

Other rare earths and transition metals specially Iron badly affect the proposed amperometric estimation procedure. Ions like halides and nitrates also interfere the said procedure.

Under optimum conditions as described above 1, 10 phenanthroline has proved to be a selective reagent to detect the trace quantity of rare earths as low as 1.6 mg of each ion with experimental error less than 1% in each case. The statistical data also support the above view.

**Table 4.1: Amperometric titration of Zr(IV) with PAN at -0.60 V vs
SCE at pH - 3.1±0.1, $\mu = 0.1 \text{ mol dm}^{-3}$ KCl**

| S. No. | Approximate concentration Zr(IV) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|---|------------------------------------|------------------------------------|----------------|
| 1. | 1.0×10^{-4} | 0.9122 | 0.9212 | 0.99 |
| 2. | 1.5×10^{-4} | 1.3683 | 1.3815 | 0.97 |
| 3. | 2.0×10^{-4} | 1.8244 | 1.8424 | 0.99 |
| 4. | 2.5×10^{-4} | 2.2805 | 2.3017 | 0.93 |
| 5. | 3.0×10^{-4} | 2.2805 | 2.3017 | 0.93 |
| 6. | 3.5×10^{-4} | 3.1927 | 3.2195 | 0.84 |

Average mean deviation from practical error = 1.43%

Standard deviation = 0.01

Coefficient of variance (C.V.) = 0.23%

**Table 4.2 : Amperometric titration of Tb(III) with 1,(2-Pyridyl
azo) 2-Naphthol at - 0.60 V vs SCE at pH - 3.1 ± 0.1,
μ = 0.1 mol dm⁻³ KCl.**

| S. No. | Approximate concentration Tb(III) (mol dm⁻³) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|--|------------------------------------|------------------------------------|----------------|
| 1. | 1x 10 ⁻⁴ | 1.6000 | 1.6131 | 0.82 |
| 2. | 2 x 10 ⁻⁴ | 3.2000 | 3.2265 | 0.83 |
| 3. | 3 x 10 ⁻⁴ | 4.8000 | 4.8388 | 0.81 |
| 4. | 4 x 10 ⁻⁴ | 6.4000 | 6.4464 | 0.73 |
| 5. | 5 x 10 ⁻⁴ | 8.000 | 8.4592 | 0.74 |
| 6. | 6 x 10 ⁻⁴ | 9.6000 | 9.6681 | 0.71 |
| 7. | 7 x 10 ⁻⁴ | 11.2000 | 11.2772 | 0.69 |
| 8. | 8 x 10 ⁻⁴ | 12.8000 | 12.8832 | 0.65 |
| 9. | 9 x 10 ⁻⁴ | 14.4000 | 14.5166 | 0.81 |
| 10. | 10 x 10 ⁻⁴ | 16.0000 | 16.1152 | 0.72 |

Average mean deviation from practical error = 0.4%

Standard deviation = 0.021

Coefficient of variance (C.V.) = 0.22%

Table 4.3 : Amperometric titration of Dy(III) with 1, (2-Pyridyl azo) 2-Naphthol at -0.60 V vs SCE at pH - 3.1± 0.1, $\mu = 0.1 \text{ mol dm}^{-3} \text{ KCl}$

| S. No. | Approximate concentration Dy(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|--|-----------------------------|-----------------------------|---------|
| 1. | 1×10^{-4} | 1.6250 | 1.61264 | 0.79 |
| 2. | 2×10^{-4} | 3.2500 | 3.2753 | 0.78 |
| 3. | 3×10^{-4} | 4.8750 | 4.8379 | 0.79 |
| 4. | 4×10^{-4} | 6.500 | 6.5494 | 0.76 |
| 5. | 5×10^{-4} | 8.1250 | 8.1825 | 0.77 |
| 6. | 6×10^{-4} | 9.7500 | 9.8241 | 0.76 |
| 7. | 7×10^{-4} | 11.3750 | 11.4545 | 0.78 |
| 8. | 8×10^{-4} | 13.0000 | 13.0845 | 0.65 |
| 9. | 9×10^{-4} | 14.6250 | 14.731 | 0.76 |
| 10. | 10×10^{-4} | 16.2500 | 16.3702 | 0.74 |

Average mean deviation from practical error = 0.65%

Standard deviation = 0.007

Coefficient of variance (C.V.) = 0.12%

Table 4.4 : Amperometric titration of Er(III) with 1, (2-Pyridyl azo) 2-Naphthol at - 0.60 V vs SCE at pH - 3.1± 0.1, $\mu = 0.1 \text{ mol dm}^{-3} \text{ KCl}$

| S. No. | Approximate concentration Er(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|--|-----------------------------|-----------------------------|---------|
| 1. | 1×10^{-4} | 1.672 | 1.6806 | 0.52 |
| 2. | 1.2×10^{-4} | 2.0064 | 2.0168 | 0.54 |
| 3. | 1.3×10^{-4} | 2.1736 | 2.1859 | 0.55 |
| 4. | 1.4×10^{-4} | 2.338 | 2.3517 | 0.59 |
| 5. | 1.5×10^{-4} | 2.5050 | 2.5180 | 0.52 |
| 6. | 1.6×10^{-4} | 2.6720 | 2.6864 | 0.54 |
| 7. | 1.7×10^{-4} | 2.8434 | 2.8564 | 0.53 |
| 8. | 1.8×10^{-4} | 3.0096 | 3.0183 | 0.61 |
| 9. | 1.9×10^{-4} | 3.1768 | 3.1968 | 0.63 |
| 10. | 2×10^{-4} | 3.344 | 3.3637 | 0.59 |

Average mean deviation from practical error = 2.61%

Standard deviation = 0.007

Coefficient of variance (C.V.) = 0.29%

Table 4.5: Amperometric titration of Sm(III) with PAN at -0.60**V vs SCE at pH - 3.1+0.1, $\mu = 0.1 \text{ mol dm}^{-3}$ KCl**

| S. No. | Approximate concentration Sm(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|--|------------------------------------|------------------------------------|----------------|
| 1. | 1.0×10^{-4} | 1.5030 | 1.5166 | 0.91 |
| 2. | 1.5×10^{-4} | 2.2500 | 2.2709 | 0.93 |
| 3. | 2.0×10^{-4} | 3.0000 | 3.0279 | 0.93 |
| 4. | 2.5×10^{-4} | 3.7000 | 3.7340 | 0.92 |
| 5. | 3.0×10^{-4} | 4.5000 | 4.5396 | 0.88 |
| 6. | 3.5×10^{-4} | 5.250 | 5.2962 | 0.88 |

Average mean deviation from practical error = 0.83%

Standard deviation = 0.04

Coefficient of variance (C.V.) = 0.95%

Table 4.6: Amperometric titration of Zr(IV) with PAR at -0.85**V vs SCE at pH - 3.1±0.1, $\mu = 0.1 \text{ mol dm}^{-3}$ KCl**

| S. No. | Approximate concentration Zr(IV) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|---|------------------------------------|------------------------------------|----------------|
| 1. | 1.0×10^{-4} | 0.9122 | 0.9194 | 0.79 |
| 2. | 1.5×10^{-4} | 1.3683 | 1.3796 | 0.83 |
| 3. | 2.0×10^{-4} | 1.8244 | 1.8391 | 0.81 |
| 4. | 2.5×10^{-4} | 2.2805 | 2.3012 | 0.91 |
| 5. | 3.0×10^{-4} | 2.7366 | 2.7579 | 0.78 |
| 6. | 3.5×10^{-4} | 3.1927 | 3.2185 | 0.81 |

Average mean deviation from practical error = 1.56%

Standard deviation = 0.01

Coefficient of variance (C.V.) = 0.22%

Table 4.7 : Amperometric titration of Tb(III) with 4- (2-pyridyl azo) Resorcinol at -0.85 V vs SCE, pH -3.1±0.1, $\mu = 0.1 \text{ M dm}^{-3} \text{ KCl}$ 0.001% gelatin

| S. No. | Approximate concentration Tb(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|--|-----------------------------|-----------------------------|---------|
| 1. | 1×10^{-4} | 1.6000 | 1.5856 | 0.90 |
| 2. | 2×10^{-4} | 3.2000 | 3.2160 | 0.43 |
| 3. | 3×10^{-4} | 4.8000 | 4.7600 | 0.62 |
| 4. | 4×10^{-4} | 6.4000 | 6.4400 | 0.63 |
| 5. | 5×10^{-4} | 8.0000 | 8.0340 | 0.38 |
| 6. | 6×10^{-4} | 9.6000 | 9.5480 | 0.54 |
| 7. | 7×10^{-4} | 11.2000 | 11.5671 | 0.57 |
| 8. | 8×10^{-4} | 12.8000 | 12.7309 | 0.54 |
| 9. | 9×10^{-4} | 14.4000 | 14.4606 | 0.42 |
| 10. | 1×10^{-4} | 16.0000 | 16.0864 | 0.54 |

Average mean deviation from practical error = 1.0%

Standard deviation = 0.01

Coefficient of variance (C.V.) = 0.62%

Table 4.8 : Amperometric titration of Dy(III) with 4-(2-Pyridyl azo) resorcinol at -0.85 V vs SCE, pH - 3.1 ± 0.1, $\mu = 0.1 \text{ mol dm}^{-3}$ KCl.

| S. No. | Approximate concentration Dy(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|--|-----------------------------|-----------------------------|---------|
| 1. | 1×10^{-4} | 1.6250 | 1.6141 | 0.37 |
| 2. | 2×10^{-4} | 3.2500 | 3.2383 | 0.36 |
| 3. | 3×10^{-4} | 4.8750 | 4.8550 | 0.40 |
| 4. | 4×10^{-4} | 6.5000 | 6.5300 | 0.41 |
| 5. | 5×10^{-4} | 8.1250 | 8.1550 | 0.37 |
| 6. | 6×10^{-4} | 9.7500 | 9.7158 | 0.35 |
| 7. | 7×10^{-4} | 11.3750 | 11.4202 | 0.39 |
| 8. | 8×10^{-4} | 13.0000 | 13.0546 | 0.42 |
| 9. | 9×10^{-4} | 14.6250 | 14.6893 | 0.44 |
| 10. | 1×10^{-4} | 16.2500 | 16.3182 | 0.42 |

Average mean deviation from practical error = 0.12%

Standard deviation = 0.02

Coefficient of variance (C.V.) = 0.64%

Table 4.9: Amperometric titration of Er(III) with 4-(2-Pyridyl azo)**Resorcinol at - 0.85 V vs SCE, pH - 3.1 ± 0.1, $\mu = 0.1$** **mol dm⁻³ KCl**

| S. No. | Approximate concentration Er(III) (mol dm⁻³) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|--|------------------------------------|------------------------------------|----------------|
| 1. | 1 x 10 ⁻⁴ | 1.672 | 1.660 | 0.5600 |
| 2. | 1.2 x 10 ⁻⁴ | 2.0064 | 2.0164 | 0.4980 |
| 3. | 1.3 x 10 ⁻⁴ | 2.1736 | 2.1738 | 0.4690 |
| 4. | 1.4 x 10 ⁻⁴ | 2.338 | 2.352 | 0.5900 |
| 5. | 1.5 x 10 ⁻⁴ | 2.505 | 2.516 | 0.4391 |
| 6. | 1.6 x 10 ⁻⁴ | 2.672 | 2.684 | 0.449 |
| 7. | 1.7 x 10 ⁻⁴ | 2.8434 | 2.8600 | 0.6191 |
| 8. | 1.8 x 10 ⁻⁴ | 3.0096 | 3.0249 | 0.51 |
| 9. | 1.9 x 10 ⁻⁴ | 3.1768 | 3.1922 | 0.46 |
| 10. | 2 x 10 ⁻⁴ | 3.344 | 3.3540 | 0.60 |

Average mean deviation = 0.55%

Standard deviation = 0.001

Coefficient of variance (C.V.) = 0.04%

Table 4.10: Amperometric titration of Sm(III) with PAR at -0.85**V vs SCE at pH - 3.1±0.1, $\mu = 0.1 \text{ mol dm}^{-3}$ KCl**

| S. No. | Approximate concentration Sm(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|--|-----------------------------|-----------------------------|---------|
| 1. | 1.0×10^{-4} | 1.5030 | 1.5118 | 0.79 |
| 2. | 1.5×10^{-4} | 2.250 | 2.2670 | 0.79 |
| 3. | 2.0×10^{-4} | 3.0000 | 3.0243 | 0.81 |
| 4. | 2.5×10^{-4} | 3.7500 | 3.7807 | 0.82 |
| 5. | 3.0×10^{-4} | 4.5000 | 4.5373 | 0.83 |
| 6. | 3.5×10^{-4} | 5.2500 | 5.2930 | 0.82 |
| 7. | 4.5×10^{-4} | 6.7635 | 6.8026 | 0.78 |

Average mean deviation from practical error = 1.83%

Standard deviation = 0.04

Coefficient of variance (C.V.) = 0.94%

Table 4.11: Amperometric titration of Zr(IV) with methylene blue at -0.4 V vs SCE at pH - 3.1±0.1, $\mu = 0.1 \text{ mol dm}^{-3}$ KCl

| S. No. | Approximate concentration Zr(IV) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|---|------------------------------------|------------------------------------|----------------|
| 1. | 1.0×10^{-4} | 0.9122 | 0.9284 | 0.69 |
| 2. | 1.5×10^{-4} | 1.3683 | 1.3781 | 0.72 |
| 3. | 2.0×10^{-4} | 1.8244 | 1.8368 | 0.68 |
| 4. | 2.5×10^{-4} | 2.2805 | 2.2950 | 0.64 |
| 5. | 3.0×10^{-4} | 2.7366 | 2.7565 | 0.73 |
| 6. | 3.5×10^{-4} | 3.1927 | 3.2153 | 0.71 |

Average mean deviation from practical error = 1.05%

Standard deviation = 0.01

Coefficient of variance (C.V.) = 0.23%

Table 4.12 : Amperometric titrations of Tb(III) with methylene blue at -0.4 V vs SCE at pH - 3.1 ± 0.1 , $\mu = 0.1 \text{ mol dm}^{-3}$ KCl

| S. No. | Approximate concentration of Tb(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|---|-----------------------------|-----------------------------|---------|
| 1. | 1×10^{-4} | 1.60 | 1.6101 | 0.625 |
| 2. | 1.2×10^{-4} | 1.92 | 1.9319 | 0.620 |
| 3. | 1.3×10^{-4} | 2.08 | 2.0928 | 0.616 |
| 4. | 1.4×10^{-4} | 2.24 | 2.2536 | 0.610 |
| 5. | 1.5×10^{-4} | 2.40 | 2.4146 | 0.610 |
| 6. | 1.6×10^{-4} | 2.56 | 2.5748 | 0.580 |
| 7. | 1.7×10^{-4} | 2.72 | 2.7368 | 0.600 |
| 8. | 1.8×10^{-4} | 2.88 | 2.8967 | 0.580 |

Average mean deviation from practical error = 0.80%

Standard deviation = 0.004

Coefficient of variance (C.V.) = 0.15%

Table 4.13 : Amperometric titrations of Dy(III) with methylene blue at - 0.4 V vs SCE at pH - 3.1 ± 0.1, $\mu = 0.1$ mol dm⁻³ KCl

| S. No. | Approximate concentration of Dy(III) (mol dm ⁻³) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|--|-----------------------------|-----------------------------|---------|
| 1. | 1 x 10 ⁻⁴ | 1.625 | 1.6305 | 0.65 |
| 2. | 1.2 x 10 ⁻⁴ | 1.8525 | 1.8311 | 0.61 |
| 3. | 1.3 x 10 ⁻⁴ | 1.9500 | 1.9613 | 0.58 |
| 4. | 1.4 x 10 ⁻⁴ | 2.1125 | 2.1226 | 0.60 |
| 5. | 1.5 x 10 ⁻⁴ | 2.2750 | 2.2838 | 0.61 |
| 6. | 1.6 x 10 ⁻⁴ | 2.4375 | 2.4445 | 0.60 |
| 7. | 1.7 x 10 ⁻⁴ | 2.6000 | 2.6169 | 0.65 |
| 8. | 1.8 x 10 ⁻⁴ | 2.7625 | 2.7799 | 0.63 |

Average mean deviation from practical error = 0.60%

Standard deviation = 0.01

Coefficient of variance (C.V.) = 0.47%

Table 4.14: Amperometric titration of Er(III) with Methylene blue at -0.4 V vs SCE at pH - 3.1 ± 0.1 , $\mu = 0.1$ mol dm^{-3} KCl

| S. No. | Approximate concentration Er(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|--|------------------------------------|------------------------------------|----------------|
| 1. | 1×10^{-4} | 1.672 | 1.6813 | 0.56 |
| 2. | 1.2×10^{-4} | 2.0064 | 2.0164 | 0.49 |
| 3. | 1.3×10^{-4} | 2.1736 | 2.1838 | 0.47 |
| 4. | 1.4×10^{-4} | 2.338 | 2.3520 | 0.55 |
| 5. | 1.5×10^{-4} | 2.505 | 2.5160 | 0.43 |
| 6. | 1.6×10^{-4} | 2.672 | 2.6840 | 0.44 |
| 7. | 1.7×10^{-4} | 2.8434 | 2.8600 | 0.61 |

Average mean deviation from practical error = 0.38%

Standard deviation = 0.004

Coefficient of variance (C.V.) = 0.19%

Table 4.15: Amperometric titration of Sm(III) with methylene blue at -0.4 V vs SCE at pH - 3.1±0.1, $\mu = 0.1 \text{ mol dm}^{-3}$ KCl

| S. No. | Approximate concentration Sm(III) (mole dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|---|------------------------------------|------------------------------------|----------------|
| 1. | 1.0×10^{-4} | 1.503 | 1.5126 | 0.64 |
| 2. | 1.5×10^{-4} | 2.250 | 2.2646 | 0.65 |
| 3. | 2.0×10^{-4} | 3.000 | 3.0180 | 0.60 |
| 4. | 2.5×10^{-4} | 3.700 | 3.7214 | 0.58 |
| 5. | 3.0×10^{-4} | 4.500 | 4.5288 | 0.64 |
| 6. | 3.5×10^{-4} | 5.250 | 5.2846 | 0.66 |

Average mean deviation from practical error = 0.58%

Standard deviation = 0.01

Coefficient of variance (C.V.) = 0.49%

Table 4.16 : Amperometric titration of Tb(III) with 1,10 phenanthroline at - 1.42V vs SCE at pH -3.1± 0.1, $\mu = 0.1 \text{ mol dm}^{-3} \text{ KCl}$

| S. No. | Approximate concentration Tb(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|--|------------------------------------|------------------------------------|----------------|
| 1. | 1×10^{-4} | 1.600 | 1.6081 | 0.51 |
| 2. | 2×10^{-4} | 3.200 | 3.2169 | 0.53 |
| 3. | 3×10^{-4} | 4.800 | 4.823 | 0.49 |
| 4. | 4×10^{-4} | 6.400 | 6.433 | 0.52 |
| 5. | 5×10^{-4} | 8.00 | 8.045 | 0.58 |
| 6. | 6×10^{-4} | 9.60 | 9.657 | 0.60 |
| 7. | 7×10^{-4} | 11.2 | 11.270 | 0.63 |
| 8. | 8×10^{-4} | 12.8 | 12.849 | 0.39 |
| 9. | 9×10^{-4} | 14.4 | 14.454 | 0.38 |
| 10. | 10×10^{-4} | 16.0 | 16.528 | 0.33 |

Average mean deviation from practical error = 0.93%

Standard deviation = 0.10

Coefficient of variance (C.V.) = 2.11%

Table 4.17 : Amperometric titration of Dy(III) with 1, 10 phenanthroline at -1.42 V vs SCE at pH - 3.1± 0.1, $\mu = 0.1 \text{ mol dm}^{-3} \text{ KCl}$

| S. No. | Approximate concentration Dy(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|--|-----------------------------|-----------------------------|---------|
| 1. | 1×10^{-4} | 1.6250 | 1.635 | 0.61 |
| 2. | 2×10^{-4} | 3.250 | 3.265 | 0.46 |
| 3. | 3×10^{-4} | 4.875 | 4.89 | 0.51 |
| 4. | 4×10^{-4} | 6.500 | 6.53 | 0.52 |
| 5. | 5×10^{-4} | 8.1250 | 8.07 | 0.53 |
| 6. | 6×10^{-4} | 9.7500 | 9.75 | 0.51 |
| 7. | 7×10^{-4} | 11.3750 | 11.43 | 0.52 |
| 8. | 8×10^{-4} | 13.0000 | 13.07 | 0.54 |
| 9. | 9×10^{-4} | 14.6250 | 16.54 | 0.53 |
| 10. | 1×10^{-4} | 16.2500 | 16.07 | 0.48 |

Average mean deviation from practical error = 0.65%

Standard deviation = 0.10

Coefficient of variance (C.V.) = 1.70%

Table 4.18 : Amperometric titration of Er(III) with 1, 10, phenanthroline at -1.42 V vs SCE at pH - 3.1± 0.1, $\mu = 0.1 \text{ mol dm}^{-3} \text{ KCl}$

| S. No. | Approximate concentration Er(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|--------|--|-----------------------------|-----------------------------|---------|
| 1. | 1×10^{-4} | 1.672 | 1.6805 | 0.63 |
| 2. | 1.2×10^{-4} | 2.0064 | 2.0148 | 0.74 |
| 3. | 1.3×10^{-4} | 2.1736 | 2.1832 | 0.61 |
| 4. | 1.4×10^{-4} | 2.338 | 2.3432 | 0.60 |
| 5. | 1.5×10^{-4} | 2.5050 | 2.515 | 0.60 |
| 6. | 1.6×10^{-4} | 2.6720 | 2.6865 | 0.60 |
| 7. | 1.7×10^{-4} | 2.8434 | 2.8567 | 0.59 |
| 8. | 1.8×10^{-4} | 3.0096 | 3.0144 | 0.48 |
| 9. | 1.9×10^{-4} | 3.1768 | 4.121 | 0.30 |
| 10. | 2×10^{-4} | 3.344 | 3.3510 | 0.33 |

Average mean deviation from practical error = 0.46%

Standard deviation = 0.003

Coefficient of variance (C.V.) = 0.13%

Table 4.19 : Amperometric titration of Sm(III) with 1, 10 phenanthroline at -1.42 V vs SCE at pH -3.1±0.1, $\mu = 0.1 \text{ mol dm}^{-3} \text{ KCl}$

| S. No. | Approximate concentration Sm(III) (mol dm^{-3}) | Amount of metal taken (mg.) | Amount of metal found (mg.) | % Error |
|---------------|--|------------------------------------|------------------------------------|----------------|
| 1. | 1.0×10^{-4} | 1.503 | 1.5153 | 0.82 |
| 2. | 1.5×10^{-4} | 2.250 | 2.2664 | 0.73 |
| 3. | 2.0×10^{-4} | 3.000 | 3.0222 | 0.74 |
| 4. | 2.5×10^{-4} | 3.700 | 3.7340 | 0.92 |
| 5. | 3.0×10^{-4} | 4.500 | 4.5432 | 0.96 |
| 6. | 3.5×10^{-4} | 5.250 | 5.2935 | 0.83 |

Average mean deviation from practical error = 0.56%

Standard deviation = 0.004

Coefficient of variance (C.V.) = 0.18%

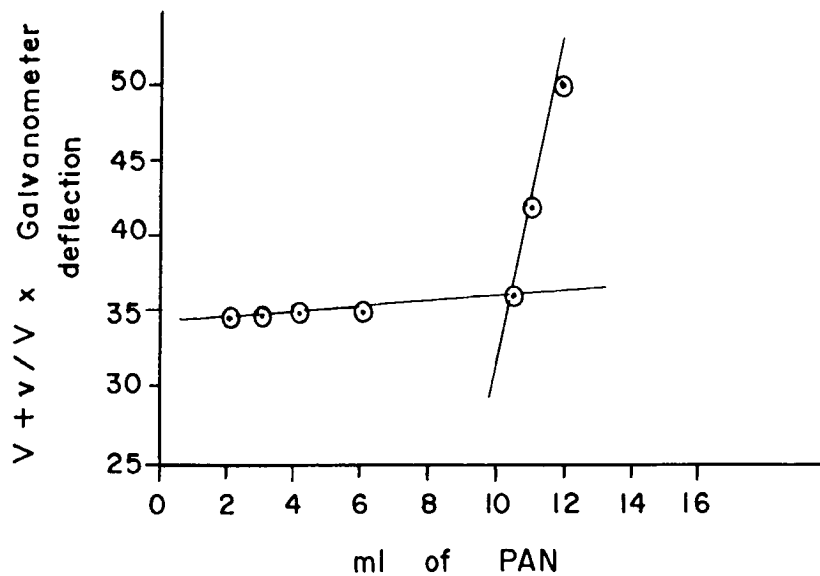


Fig.4.01 :An Amperometric titration curve of Tb^{3+} ion 1mM/100ml with 0.1mM / ml PAN

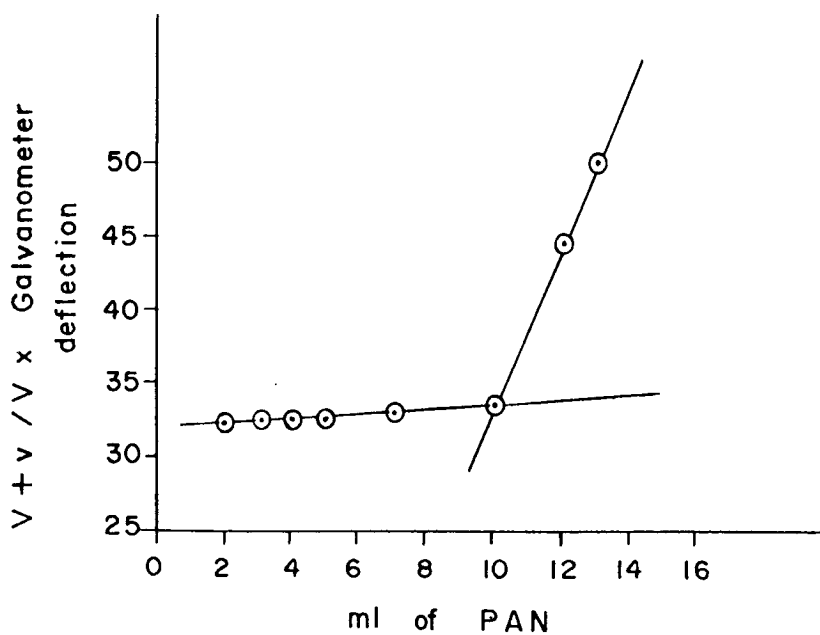


Fig. 4.02 : An Amperometric titration curve of Dy^{3+} ion 1mM/100ml with 0.1 mM/ml PAN

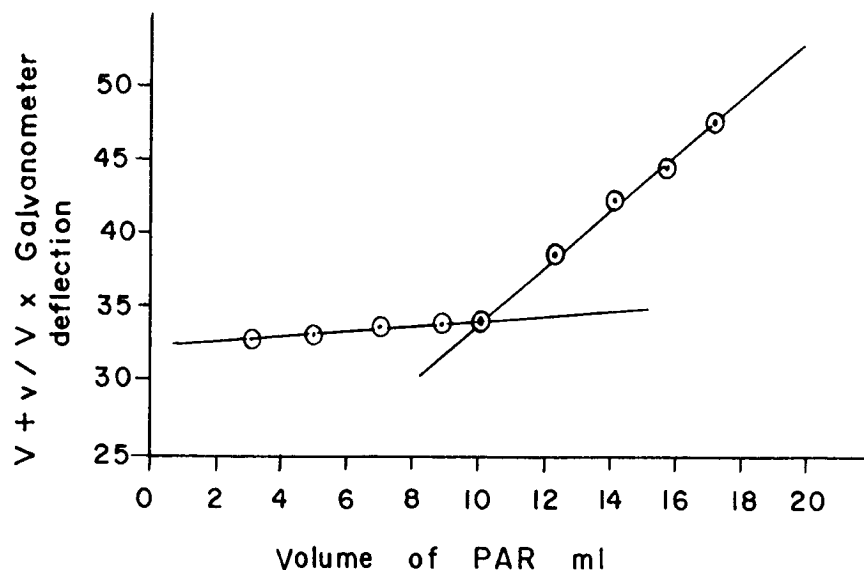


Fig. 4.03 : An Amperometric titration curve of Tb^{3+}
 1mM/100ml with 0.1 mM / ml PAR

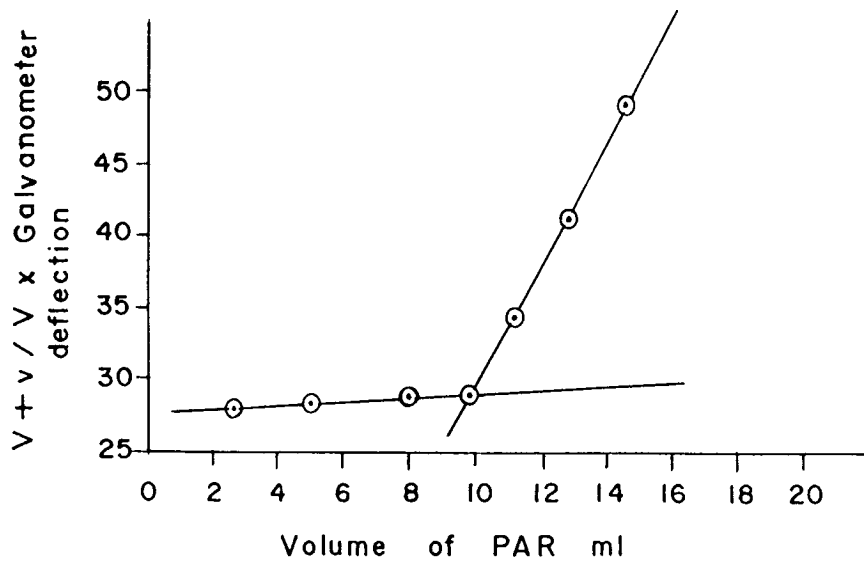


Fig.4.04 : An Amperometric titration curve of Dy^{3+}
 1mM /100ml with 0.1 mM / ml PAR

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