CHAPTER SIX

AMPEROMETRIC ESTIMATIONS OF TRIVALENT
La, Ce, Pr and Nd WITH SOME AZO DYES
The current-voltage behaviour of an electro-active substance, in majority of cases, depends upon the fact that the diffusion current is proportional to its concentration in the solution, and if some of the electro-active material is removed by interaction with another reagent there would be a decrease in the diffusion current. This is the fundamental principle of amperometric titrations. Hence the observed diffusion current at a suitable applied potential is measured as a function of the volume of the titrating solution, and the end point is the point of intersection of two lines giving the change of current before and after the equivalence point. Thus in amperometric titrations, the current which passes through the titration cell between an indicator electrode the DME and reference electrode SCE, at a suitable applied emf, is measured as a function of the volume of the titrating solution. Polarometric and polarographic are the other terms used for amperometric titrations. These titrations are advantageous over conventional potentiometric and conductometric titrations, in the accuracy and precision of the results.

A survey of literature reveals that the first amperometric titration was performed by Heyrovsky and Berezicky ¹. Since then the technique has been employed successfully to estimate various cations and anions ²-⁸. However, very few references are available on the amperometric estimation of rare earths.
Misumi and Iwase \(^9\) estimated rare earths amperometrically with EDTA and reported \(11\) chelate formation in each case.

Lanthanum as fluoride has been estimated amperometrically by Yamashita with iron (III) as the indicator ion \(^{10}\).

Vanadyl sulphate solution, used by Goldstein et al. \(^{11}\) as a back titrant for EDTA, permitted the indirect determination of lanthanones. The titration has been carried out at the optimum pH 4.0 ± 0.5, with a potential of -0.6 V applied to a platinum electrode of area \(1 \text{ sq.cm.}\)

Lighter lanthanides have been determined amperometrically by cupferron \(^{12}\), in an ammonical acetate medium of pH 3.6 to 6. The plateau potential on the cupferron wave applied was -1.2 V using rotating platinum anode vs a stationary platinum cathode system. The stoichiometry of the complexes formed was 1:4. However, Pitre and Lavale \(^{13,14}\) determined La, Ce, Pr and 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. The stoichiometry of the complexes was found to be \(111\).

Gaur and Zutshi \(^{15}\) have titrated air-free \(0.001\) to \(0.02 \text{ mol dm}^{-3}\) lanthanum nitrate solution with potassium ferrocyanide solution and concluded that the compound
LaK | Fe(CN)$_6$ | was formed. This titration produced an L-shaped curve and was presumably carried out at a DME potential of $-1.85$ V vs SCE.

Ce(III) has been estimated amperometrically with potassium ferricyanide in potassium carbonate solution using a rotating platinum electrode. In this method Ce(IV) did not interfere.

Varma has used Fe(III) indicator electrode to titrate Ce(III) with fluoride ion in an ammonium chloride-acetate medium that contained an equal volume of 96% ethanol at pH $6.2 \pm 0.02$.

Saxena and Mittal found that amperometric titration with molybdate ion gave good results with Ce(III) concentration as low as $0.001$ mol dm$^{-3}$. The precipitate obtained at pH $6.0 \pm 0.2$ corresponds to the composition Ce$_2$O$_3$.3 MoO$_3$.

Maier and Swift attempted to determine Mn(II), As(III) and Ce(III) biamperometrically with electrolytically generated Ag(II) ion.

Goffart has titrated Ce(III) at a concentration of about $0.5$ mg/ml with permanganate ion by using platinum electrode and an internal silver-silver chloride electrode system that were connected together through a
galvanometer. The medium was saturated by sodium pyrophosphate solution and its pH adjusted between 7 and 8 by the addition of dilute hydrochloric acid.

Kolthoff and Jacobson 22 have performed the permanganate titration of Ce(III) ion in 0.25 mol dm⁻³ pyrophosphate buffers at pH 5 and 8 at a rotating platinum electrode of zero potential.

Recently Pitre and Lavale has reported the amperometric estimations of some lanthanides with ARS, PAR, PAN, and xylene orange 23-25.

Thus a survey of literature reveals that tartrazine and naphthaline scarlet 4RS, basic azo dyes, with form beautiful colored lakes with metal ions have not been used for amperometric estimations of rare earths. The present chapter deals with amperometric estimations of tartrazine (TZE) and naphthaline scarlet 4RS, with trivalent La, Ce, Pr and Nd.

**EXPERIMENTAL**

All the chemicals used were of AnalR/PCX grade. Stock solutions of tartrazine and naphthaline scarlet 4RS (0.01 mol dm⁻³) (ICI, India) were prepared by direct weighing the requisite quantity of the chemicals in doubly distilled water. Lanthanum(III) nitrate (Riedel, Hungary) solution (0.01 mol dm⁻³) was also prepared by direct
weighing the requisite chemical in doubly distilled water and was standardized. Ammonium hydroxide and ammonium chloride (2.0 mol dm\(^{-3}\)) solutions were prepared in distilled water, to be used as buffers. The solutions of Ce(III) chloride, Pr(III) chloride, Nd(III) chloride, potassium chloride and gelatin were prepared as mentioned in chapter II, page 47.

In each case preliminary experimental sets were prepared by keeping over all concentrations of potassium chloride and gelatin fixed at 0.1 mol dm\(^{-3}\), 0.01% gelatin containing known amounts of the metal ions (in 10 ml volume). Ammonium chloride and ammonium hydroxide solutions were used as buffers, to adjust the pH of test solutions at 8.20 ± 0.1 and 8.10 ± 0.1 for tartrazine and naphthalene scarlet 4RS respectively. The pH of the test solutions was measured on an Elico digital pH meter (model E 120). The ionic strength \(\mu = 0.3\) was maintained by the addition of potassium chloride. Pure nitrogen gas was passed through test solutions for ten minutes for deaeration.

Polarographic behaviour of tartrazine and naphthalene scarlet 4RS were studied on a CIC (Verna, India) automatic pen recording polarograph, whereas, amperometric titrations were performed on a manually operated polarograph with multiflex galvanometer (sensitivity \(8.10 \times 10^{-9}\) ampere/div) using DME as indicator electrode and mercury pool as reference electrode. The capillary characteristics were
POTENTIAL V vs SCE

Polarogram of 1.0 m mol dm$^{-3}$ Tartrazine in 0.1 mol dm$^{-3}$ KCl + 0.01% gelatin at pH 8.2 ± 0.1, adjusted with Ammonium Chloride and Ammonium hydroxide buffers.
\[ m = 2.37 \text{ mg s}^{-1}, \quad t = 3.0 \text{ s} \] at 35 cm effective height of the mercury head.

**TARTRAZINE AS AN AMPEROMETRIC REAGENT**

Tartazine [the tri sodium salt of 5-azo-4-(p-sulphophenylazo)-1-(p-sulphophenyl)-2-pyrazolin-3-carboxylic acid] is a basic azo dye (acid yellow CI 19140) used for dyeing food stuffs and preservatives. It has also been used as a redox indicator and as sodium salt in inks. It shows a yellow to purple colour change with pH, which may be used to explore the possibility of its being used as a metallochromic indicator. It has also been used as an amperometric titrant for the study of Zr(IV).

Recently Limaye and Saxena have reported 1:1 binary complexes of tartazine with some trivalent La, Ce, Pr, Nd and Sm pH metrically.

The current-voltage behaviour of tartazine was studied on a CIC (Baroda, India) automatic pen recording polarograph with DME as indicator and SCE as reference electrode. It was observed that tartazine gave a well-defined reduction wave in ammonium chloride and ammonium hydroxide buffer at pH value 3.20 ± 0.1 with \( E_{1/2} = -0.68 \text{ V} \) vs SCE and the wave height was found to be proportional to the concentration of the dye. [Fig. 6.1] The plateau potential on the wave = -0.82 V vs SCE was applied for carrying out the amperometric titrations, as done by Popa et.al., who
Amperometric Titration Curve of Pr(III) solution vs Tartrazine.

Concentration of Tartrazine taken in Cell = 2 m mol dm$^{-3}$ and concentration of Pr(III) ≠ 2 m mol dm$^{-3}$/ml.
have estimated Zr(M) with tartrazine at - 0.90 V vs SCE with an error of 2% in nitric acid as a supporting electrolyte.

After fixing the desired plateau potential, the amperometric titrations were performed by adding a standard solution of metal ion drop by drop from a semi micro burette (1.0 cm³) and the current was noted, a yellow coloured precipitate was formed. On plotting the galvanometer readings after necessary volume corrections against titrant volumes, L-shaped curve [Fig. 6.2], was obtained. The end point indicated a metal to tartrazine ratio of 1:1, which is in good agreement with the pH metric studies of Limaye and Saxena 30. Under the identical experimental conditions, similar results were obtained by choosing tartrazine as titrant and metal solutions understudy as titrate. In the latter case a reversed L-shaped curve was obtained. The data presented in table 6.1 and 6.2 clearly indicate that this method can be successfully applied for the estimation of trace amount of the titled metal ions, with an error less than ±0.53%. The accuracy and precision of the method was also studied.

Study of Effect of Diverse Ions

For interfering studies, known amounts of some foreign ions were added to a definite amount of metal ion,
FIG. 6.3

POTENTIAL V vs SCE

Polarogram of 1.0 m mol dm$^{-3}$ Naphthaline Scarlet 4RS in 0.1 mol dm$^{-3}$ KCl + 0.01% gelatin at pH 8.1 ± 0.1, adjusted with Ammonium Chloride and Ammonium Hydroxide buffers.
and the metal was titrated as described above. It was observed that the titrations of trivalent La, Ce, Pr and Nd were not anyway hampered by the presence ions like Cl\(^-\), Br\(^-\), I\(^-\), SO\(_4\)^\(-\), NO\(_3\)^\(-\), CH\(_3\)COO\(^-\), NH\(_4\)^\(+\), alkali and alkaline earth metals. However, Zr(IV), Hf(IV) and other lanthanides, Ba\(^{2+}\), Pb\(^{2+}\) and VO\(_3\)^\(-\) seriously interfered in the titrametric procedure.

NAPHTHALINE SCARLET 4RS AS AN AMPEROMETRIC REAGENT

Naphthaline scarlet 4RS forms brilliant scarlet lakes with various metal ions. It shows a colourless to red colour change with pH (red in acid medium and colourless in alkaline medium), which may find its use as a metallochromic indicator. However, no attempt seems to have been made to study its complexes.

The polarograms of naphthaline scarlet 4RS have been studied in ammonium chloride and ammonium hydroxide buffers at pH 6.1 ± 0.1. It gave a well defined reduction wave with \(E_{1/2} = -0.65\) V vs SCE [Fig. 6.3]. The wave height was proportional to the concentration. For amperometric titrations the plateau potential on the wave = -0.65 V vs Hg pool anode was applied. The current volume titration curves were well defined, indicating 1:1 stoichiometric ratio for the metal reagent complexation in each case. The titration procedure was similar as described earlier. The current-volume curves are given in Fig. 6.4. An orange red coloured
Amperometric Titration Curve of La(III) solution vs Naphthaline scarlet 4RS.

Concentration of Naphthaline Scarlet 4 RS taken in Cell = 1.0 m mol dm$^{-3}$ and concentration of La(III) = 1.0 m mol dm$^{-3}$/ml.
precipitate was formed with each of the stated metal ion. The data depicted in table 6.3 and 6.4 clearly indicate that this method can be successfully employed for the trace estimations of trivalent La, Ce, Pr and Nd, with an error of less than 0.8%. The accuracy and precision of the method has also been reported.

Study of Effect of Diverse Ions

It was observed that the titration for these metal ions was not in anyway hampered by the presence of fairly large amount of ions like halides, \( \text{SO}_4^{2-} \), \( \text{PO}_4^{3-} \), \( \text{CH}_3\text{COO}^- \), \( \text{NO}_3^- \), \( \text{NH}_4^+ \), alkali and alkaline earth metal ions. However, \( \text{Ba}^{2+} \), \( \text{Pb}^{2+} \), \( \text{Ga}^{3+} \), \( \text{In}^{3+} \) and \( \text{Hf}^+ \), other lanthanides seriously interfered in the titrometric procedure.
### TABLE - 6.1

Amperometric determination of La(III) and Ce(III) with Tartrazine

Plateau Potential = $-0.82$ V vs Hg pool; $\mu = 0.3$

<table>
<thead>
<tr>
<th>Concentration (mmol dm$^{-3}$)</th>
<th>Amount of La(III) Taken (mg)</th>
<th>Amount of La(III) Found (mg)</th>
<th>$%$ error</th>
<th>Coefficient of variation</th>
<th>Amount of Ce(III) Taken (mg)</th>
<th>Amount of Ce(III) Found (mg)</th>
<th>$%$ error</th>
<th>Coefficient of variation</th>
</tr>
</thead>
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<tr>
<td>0.5</td>
<td>0.6945</td>
<td>0.6917</td>
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<td>0.7007</td>
<td>0.6982</td>
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<td>1.4012</td>
<td>1.4084</td>
<td>+0.51</td>
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<td>2.1018</td>
<td>2.1026</td>
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<td>0.18</td>
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Average mean deviation = 0.31%
Average Standard deviation = 0.27%

Average mean deviation = 0.22%
Average Standard deviation = 0.18%
### TABLE - 6.2

**Amperometric determination of Pr(III) and Nd(III) with Tartrazine**

Plateau Potential = -0.82 V vs Hg pool; $\mu = 0.3$

<table>
<thead>
<tr>
<th>Concentration (mol dm$^{-3}$)</th>
<th>Amount of Pr(III) Taken (mg)</th>
<th>% error</th>
<th>Coefficient of variation</th>
<th>Amount of Pr(III) Found (mg)</th>
<th>% error</th>
<th>Coefficient of variation</th>
<th>Amount of Nd(III) Taken (mg)</th>
<th>% error</th>
<th>Coefficient of variation</th>
<th>Amount of Nd(III) Found (mg)</th>
<th>% error</th>
<th>Coefficient of variation</th>
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<td>0.7046</td>
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<td></td>
<td>0.7010</td>
<td>-0.51</td>
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<td>0.7190</td>
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Average mean deviation = 0.40%
Average Standard deviation = 0.36%

Average mean division = 0.42%
Average Standard deviation = 0.38%
### TABLE - 6.3

Amperometric determination of La(III) and Ce(III) with Naphthalene Stark 4 RS
Plateau Potential = -0.85 V vs Hg pool; \( \mu = 0.3 \)

<table>
<thead>
<tr>
<th>Concentration m mol dm(^{-3})</th>
<th>Amount of La(III)</th>
<th>% error</th>
<th>Coefficient of variation</th>
<th>Amount of Ce(III)</th>
<th>% error</th>
<th>Coefficient of variation</th>
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<td></td>
<td>Taken (mg)</td>
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Average mean deviation = 0.30%  
Average Standard deviation = 0.28%

Average mean deviation = 0.28%  
Average Standard deviation = 0.23%
## TABLE - 6.4

Amperometric determination of Pr(III) and Nd(III) with Naphthaline Scarlet 4RS

Plateau Potential = -0.85 V vs Hg pool; \( \mu = 0.3 \)

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<th>Concentration (mmol dm(^{-3}))</th>
<th>Amount of Pr(III) Taken (mg)</th>
<th>Amount of Pr(III) Found (mg)</th>
<th>Error (%)</th>
<th>Coefficient of Variation</th>
<th>Amount of Nd(III) Taken (mg)</th>
<th>Amount of Nd(III) Found (mg)</th>
<th>Error (%)</th>
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<td>0.7212</td>
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Average mean deviation = 0.36%  
Average Standard deviation = 0.32%

Average mean deviation = 0.26%  
Average Standard deviation = 0.22%
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14. K.S. Pitre and S.C. Lavale,

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17. A.K. Zhdanov and N.A. Kurochkina,

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25. S.C. Lavale and K.S. Pitre,

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27. A. Butucella,
28. Ju. Lurie,

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