The importance of low concentrations has tremendously increased both in science and technology in recent years. Quantitative determination of very dilute solutions is now required in all the fields of activity associated with high purity substances including research, manufacture and utilization. It is certain that future developments in science and technology will make still higher demands on low concentration analysis, so that new methods will be necessary. In this field, amperometry has proved a very useful technique. Amperometric titrations have a wide field of applicability and accuracy of a few tenth of a percent is commonly attainable with solutions of concentrations as low as $10^{-4}$ M; more dilute solutions up to $10^{-5}$ M have often been estimated within the inaccuracy limit of ±2%. The present work deals with the evolution of successful amperometric methods of determination of thirteen metal ion species, viz. V(V), Cr(VI), Mn(VII), Fe(III), Co(III), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Pt(IV), Ag(I) and Au(III). Two organic ligands, thiomalic acid (TSH) and thiodipropionic acid (TDFS) have been used as reagents for accomplishing this work in view of their strong tendency to enter into coordination with the metal ions as well as their susceptibility to undergo oxidation by some of them. TSH is also known to be polarographically active and gives an anodic wave pertaining to its one electron oxidation at d.m.e. TDFS does not give any wave.
A brief, chapter-wise resume of the thesis is as follows:

**INTRODUCTION**

This chapter opens with a brief history of evolution and salient features of the technique of amperometry. Description of electrodes other than d.m.e., used in this work, has been given and their merits and demerits discussed in short. Aims, objectives and the scope of the present work have been defined under the sub-heading "Current importance of low concentrations and the present work." A survey of literature published on the amperometric determination of various metal species, chosen by the author (mentioned earlier), has also been included. This has been followed by a discussion of complexing and polarographic properties of the two ligands, TSH and TDPS. The past work on the complexation reactions of these has also been mentioned.

**METHOD, APPARATUS AND CHEMICALS**

This chapter deals with the methodology of the work and also includes a description of the dropping mercury electrode assembly and other apparatus and instruments used for investigations. Source compounds of various metal ion species determined and the methods employed for the standardization of their solutions have been mentioned. A list of source compounds of the species, whose interference in the new titrimetric methods evolved has been checked, is also given.
PART-I: TITRATIONS INVOLVING THIOMALIC ACID

Section 1: Amperometric determination of Vanadium

This section deals with the method evolved for the determination of pentavalent vanadium in the form of \( \text{VO}_3^- \) ion. The anodic wave of TSH in 0.1M KCl medium has been exploited for the purpose. Titration with V(V) solution at 0.6V results in up-side-down L-shaped titration curve which yields a V(V)-TSH molar reaction ratio of 1:2. Cent-percent results have been obtained in the vanadate concentration range of \( 5 \times 10^{-3} \text{M} - 5 \times 10^{-1} \text{M} \). It has been proposed that two TSH enter into chelation with V(V), each employing its both carboxylate groups; -SH group remains intact. The composition of the complex ion has been given as: \( [\text{VO}_2(\text{TSH})_2]^{3-} \).

Section 2: Amperometric determination of Chromium

This section deals with the new method evolved for the amperometric determination of hexavalent chromium in the form of dichromate ion. TSH gives its usual anodic wave in 1M \( \text{NH}_3-\text{NH}_4\text{Cl} \) medium with the diffusion region stretching from -0.2V to -0.4V. Dichromate gives two irreversible cathodic waves in this medium. The diffusion region of the first wave (\( E_{1/2} = -0.24V \)) is from -0.4V to -1.3V and that of the second wave (\( E_{1/2} = -1.45V \)), from -1.5V to -1.6V. The diffusion current constant of the first wave is exactly eight times that of the TSH wave. On titrating TSH solution with dichromate at -0.4V, anodic current is progressively compensated by the cathodic current of the first wave of Cr(VI). The titration curve is strictly linear and reaches the end point i.e. intersects the residual current line when the
molar concentration ratio of dichromate and TSH is 1:3. This gives the Cr(VI)-TSH ratio as 1:3. No chemical reaction between the two seems to be involved. Experimental evidences in support of this have been cited. The method enables the estimation of dichromate solution in the concentration range of \(5 \times 10^{-3} \text{M} - 8 \times 10^{-5} \text{M}\) with total accuracy.

**Section 3: Amperometric determination of Manganese**

This section deals with the methods evolved to determine Mn(VII) in the form of \(\text{MnO}_4^-\) ion with the help of TSH. The methods include both, those involving the cathodic waves of the metal species (cathodic titrations) and those involving the anodic wave of TSH (anodic titrations). Anodic titrations can be carried out in two media, 1M \(\text{Na}_2\text{SO}_4 - \text{NaHCO}_3\) (medium-i) and 0.5M \(\text{NH}_3 - \text{NH}_4\text{Cl}\) (medium-ii). In both media, \(\text{MnO}_4^-\) gives two reduction waves, the first starting at a potential more positive than 0.0V and the second at a very negative potential. It has been suggested that the first wave is due to the reduction of Mn(VII) to Mn(VI) and the second, due to the reduction of Mn(VI) to Mn(V). TSH also gives its anodic wave in both media with the diffusion region from -0.2V to -0.4V. On titrating its solution with Mn(VII) at -0.3V, anodic limiting current decreases linearly. The decrease in current, however, becomes sluggish near the residual current line (zero line). A traditional amperometric curve with the two arms intersecting each other at the null point is not obtained in this case. But the anodic arm representing the above-mentioned linear decrease in the limiting current of TSH intersects the
zero line, on being extrapolated to a slight extent, at the exact MnO\textsuperscript{4-} - TSH molar ratio of 1:3, thus providing a method for the amperometric determination of Mn(VII). The 1:3 molar ratio has been explained. MnO\textsuperscript{4-} is known to undergo a three electron reduction in alkaline medium:

$$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightleftharpoons \text{MnO}_2 + 4\text{OH}^- \quad \cdots \ (i)$$

The electrons are provided by three TSH molecules:

$$3\text{TSH} \rightleftharpoons \frac{3}{2} \text{TS} - \text{ST} + 3\text{H}^+ + 3e^- \quad \cdots (\text{ii})$$

The reasons for not obtaining the traditional curve has been explained. The method gives good results in the MnO\textsuperscript{4-} concentration range of $5 \times 10^{-3}$ M - $2 \times 10^{-1}$ M. Cathodic titration of Mn(VII) can be carried out in the medium (iii) i.e. 0.1M borax solution. TSH and MnO\textsuperscript{4-} give waves as in case of medium (i) and (ii). However, in this medium the first wave of MnO\textsuperscript{4-} is suspected to be due to the reduction of Mn(VII) to Mn(II) and the second, due to further reduction of resultant species to Mn(Hg). On titrating Mn(VII) with TSH at -0.6V, -0.8V and -1.7V, L-shaped titration curves are obtained. The above-mentioned titration voltages cover the two waves of MnO\textsuperscript{4-} though the TSH wave is absent at these. MnO\textsuperscript{4-} - TSH titrimetric molar ratio of 2:1 is obtained. This has been explained as due to the following set of reactions:

$$\text{TSH} \longrightarrow \text{TS}^* + \text{H}^+ + e^- \quad \cdots (\text{iii})$$

$$\text{MnO}_4^- + e^- \longrightarrow \text{MnO}_2^2- \quad \cdots (\text{iv})$$

$$\text{MnO}_4^- + \text{TS}^* + \text{H}^+ + \text{Hg} \longrightarrow \text{TS} - \text{MnO}_3 + \frac{1}{2}\text{Hg}_2(\text{OH})_2 \quad \cdots (\text{v})$$

Almost 100% correct results have been obtained in the MnO\textsuperscript{4-}
concentration range of $5 \times 10^{-1} \text{M} - 5 \times 10^{-5} \text{M}$. A secondary reaction between TSH and $\text{MnO}_4^-$ is also suspected, when a large excess of TSH is added. This has been proposed to be as follows:

$$2\text{TS} - \text{MnO}_4^- + 6\text{TSH} \rightarrow 1\text{TS} - \text{ST} + 2\text{MnO}_2 + 2\text{H}_2\text{O} + \text{H}_2 \quad \text{(vi)}$$

Section 4: Amperometric determination of Iron

This section deals with the new method of amperometric determination of Fe(III) in acetate buffer medium of pH 4 (total acetate concentration = 0.2M). Both the species give their waves in this medium. While TSH gives its usual anodic wave, the Fe(III) wave is proposed to be due to the following electrode reaction:

$$\text{Fe(III)} + e^- \rightarrow \text{Fe(II)} \quad \text{...(vii)}$$

The titration of TSH with Fe(III) at 0.0V and -0.05V, both voltages falling in the diffusion regions of both species, yields metal species-TSH molar reaction ratio of 1:1. The method gives good results in the Fe(III) concentration range of $5 \times 10^{-3} \text{M} - 5 \times 10^{-1} \text{M}$. It is suspected that a transitory Fe(III)-TSH complex is formed which soon yields to Fe(II) species. The coordination of TSH to Fe(III) is proposed to be through its mercaptide group and the carboxylate group farthest from sulphur.

Section 5: Amperometric determination of Cobalt

This section deals with the new methods of amperometric determination of Co(III) and Co(II). TSH gives its usual
anodic wave in 1M Na₂CO₃ - NaHCO₃ medium. On titrating TSH with [Co(NH₃)₆]³⁺ solution at -0.3V and -0.35V, a straight line curve is obtained, which intersects the residual current line at Co(III)-TSH molar concentration ratio of 1:1. Co(III) gives two cathodic waves in this medium, the first due to the reduction of Co(III) to Co(II) and the second, due to the reduction of Co(II) to Co(0). The titration voltages fall in the diffusion regions of TSH as well as the first wave of Co(III). The titration seems to be the result of gradual compensation of anodic current of TSH by the cathodic current of Co(III). No chemical interaction between the two species is indicated. Experimental evidences in support of this have been cited. The method enables the estimation of Co(III) solutions as dilute as 5x10⁻¹⁰M without any error.

New methods of amperometric estimation of Co(II) involve the use of three media: (i) 0.05M NH₃ - NH₄Cl; (ii) 0.1M Na₂CO₃-NaHCO₃; (iii) equal amounts (by volume) of 0.1M NH₃ and 0.05M (NH₄)₂C₂O₄ solutions. TSH gives its usual anodic wave with the diffusion region stretching from -0.2V to -0.4V in all the three media. On titrating its solution at -0.3V, a metal species-ligand titrimetric molar ratio of 1:2 is obtained in media (i) and (ii) and 1:1 in medium (iii). However, the titrations in the media (i) and (iii) yield good results only after the addition of some other supporting electrolyte such as KCl, KNO₃ or Na₂SO₄. It is proposed that the chelation in 1:2 complex occurs through the mercaptide group and one of the
carboxylate groups of TSH, the two ligand molecules thus occupying four coordination positions in the octahedral complex. In 1:1 complex, probably only two positions are occupied by TSH, in a similar manner. Very accurate results are obtained in all the three media.

Section 6: Amperometric determination of Nickel

This section deals with the new methods of determining Ni(II). Two concentrations (0.2M and 0.1M) of ammonia-ammonium chloride medium have been recommended for different concentrations of nickel. The titration of Ni(II) solution with TSH at -1.2V which falls in the diffusion region of the metal species (gelatin 0.005%) yields L-shaped amperometric curve which gives Ni(II)-TSH molar titrimetric ratio of 1:2. It has been proposed that the two TSH employ their both carboxylate groups, thus occupying four coordination positions; -SH group does not take part in coordination. Experimental evidences in support of this have been cited. The method enables the estimation of Ni(II) in the concentration range of 3x10⁻³M - 5x10⁻¹M in 0.2M ammonia-ammonium chloride medium while more dilute solutions can be titrated in 0.1M medium.

Section 7: Amperometric determination of Copper

This section deals with the new methods of determining Cu(II) in acetate buffer media (total concentration = 0.2M) of pH 4, 5 and 6 as well as 1M Na₂CO₃ - NaHCO₃ medium. Best
results in acetate buffer medium are obtained at pH 6. Cu(II) gives an irreversible cathodic wave in acetate buffer media, containing 0.005% gelatin, with the $E_{1/2}$ vicinity of 0.0V. The wave, in all probability, is due to the reduction of Cu(II) to Cu(0). This wave yields to amperometric titration with TSH and L-shaped titration curve is obtained at -0.4V where TSH wave is absent. The curve reveals a metal species-ligand molar reaction ratio of 1:1.25. The addition of TSH results in the emergence of a new, reversible, one electron, cathodic wave with $E_{1/2}$ value of -0.54V. The new wave in all probability, is due to the reduction of Cu(I) to Cu(Hg). It seems, one TSH reacts with one Cu(II) according to the reaction:

$$TSH + Cu(II) \rightarrow \frac{1}{2}TS - ST + Cu(I) + H^+ \quad \text{(viii)}$$

This Cu(I) in combination with more Cu(II) then forms a mixed valence complex with TSH in which Cu(II), Cu(I) and TSH may be present in the ratio of 3:1:1. The formation of this mixed valence complex along with the reaction (viii) would explain the metal species-TSH titrimetric ratio obtained. It is difficult to give an exact composition of the mixed valence complex. The Cu(I) wave, mentioned before, seems to be due to the Cu(I) of the mixed valence complex; Cu(II) of this complex does not undergo reduction at d.m.e. The titration in acetate buffer media yield good results for a fairly wide range of concentrations of Cu(II). Cu(II) gives a cathodic wave in 1M $\text{Na}_2\text{CO}_3 - \text{NaHCO}_3$ medium as well, with $E_{1/2}$ value of -0.22V. The wave is due to the reduction of Cu(II) to Cu(I). When subjected to titration with TSH at -0.8V, L-shaped curves are
obtained which yield metal species-ligand titrimetric molar ratio of 1:1.5. It seems, here too, a mixed valence complex, containing Cu(II), Cu(I) and the ligand in the ratio of 2:2:1, is formed. It is presumed that TSH brings about reduction of two Cu(II) to Cu(I) in a manner similar to that described earlier. Very accurate results have been obtained in the Cu(II) concentration range of $5 \times 10^{-3}$ - $1 \times 10^{-3}$ M.

Section 8: Amperometric determination of Zinc

This section deals with the new methods of determining Zn(II) in sodium carbonate-bicarbonate and ammonia-ammonium chloride media. Zn(II) gives an irreversible reduction wave in 1 M Na$_2$CO$_3$ - NaHCO$_3$ medium, $E_{1/2}$ value being -1.32 V. This seems to be due to the reduction of Zn(II) to Zn(0). The wave yields to titration with TSH and L-shaped amperometric curves are obtained giving Zn(II)-TSH titrimetric molar ratio of 1:3. 100% correct results have been obtained in the Zn(II) concentration range of $5 \times 10^{-3}$ - $1 \times 10^{-3}$ M. A 2-electron, reversible Zn(II) wave is obtained in ammonia-ammonium chloride medium too (containing 0.005% gelatin) and this also yields to titration with TSH. The $E_{1/2}$ values in three concentrations of the medium i.e. 1M, 0.5M and 0.3M are respectively -1.35V, -1.3V and -1.29V. Titration at -1.5V yields L-shaped curve which reveals a Zn(II)-TSH titrimetric molar ratio of 1:1. Best results are obtained in 0.5M concentration of the medium. 1:3 ratio obtained in the carbonate-bicarbonate medium seems to be due to the coordination of three ligands with one Zn(II),
each TSH employing mercaptide and one of the carboxylate
groups for the purpose. In 1:1 complex formed in the other
medium, it seems, only one TSH enters the coordination
sphere, occupying two coordination positions in the manner
described above while the remaining positions probably remain
occupied by ammonias.

Section 9: Amperometric determination of Palladium

This section deals with the new methods evolved for the
amperometric determination of Pd(II) in 0.1M KCl medium. TSH
gives its usual anodic wave in this medium while Pd(II) gives
a cathodic wave starting right from 0.0V. The cathodic wave,
in all probability, is due to the reduction of Pd(II) to
Pd(Hg). Anodic wave of TSH as well as cathodic wave of Pd(II)
can be exploited for the determination of Pd(II). The cathodic
wave, when subjected to titration with TSH yields titration
curves from which metal species-ligand ratio of 1:1 is deduced.
However, the anodic wave of TSH, when subjected to titration
at 0.0V, which falls in the diffusion region of both the
species, gives this ratio as 1:2. It has been proposed that
in this 1:2 complex, the ligand molecules coordinate with the
metal species through their mercaptide group and one of the
carboxylate groups. In 1:1 complex, only one ligand molecule
seems to enter the coordination sphere. The formation of 1:2
complex in anodic titration is probably facilitated by the
presence of TSH in excess right from the beginning. Cathodic
as well as anodic titrations yield very good results. However,
cathodic titrations are applicable to a wider range of concentrations of Pd(II) and solutions as dilute as $5.8 \times 10^{-5}$ M have been estimated with reasonable accuracy.

Section 10: Amperometric determination of Platinum

This section deals with the new method evolved for the amperometric determination of Pt(IV) in the form of $\text{PtCl}_6^{2-}$ ion in 0.1 M KCl medium. Pt(IV) gives two irreversible cathodic waves in this medium in presence of 0.005% gelatin. $E_{1/2}$ values for the first and the second waves are +0.08 V and -1.42 V respectively. In all probability, the first wave corresponds to the reduction of Pt(IV) to Pt(II) and the second, from Pt(II) to Pt(0). The first wave can be exploited for the amperometric determination of Pt(IV). Titration with TSH at -0.6 V results in L-shaped amperometric curve and a metal species-ligand molar reaction ratio of 1:1. It has been proposed that the ligand molecule coordinates through its mercaptide group and one of the carboxylate groups. Pt(IV) solutions, as dilute as $7 \times 10^{-5}$ M have been estimated with an error of less than 2%.

Section 11: Amperometric determination of Silver

This section deals with the new method evolved for the amperometric determination of Ag(I) in 0.1 M NaOH medium. TSH gives its usual anodic wave in this medium and it yields to titration with Ag(I). Titration at -0.35 V results in upside-down L-shaped amperometric curve and the
end point Ag(I)-TSH molar ratio of 1:1. It has been proposed that the complexed species formed is TS-Ag. 100% correct results have been obtained in the Ag(I) concentration range of $5 \times 10^{-3} \text{M} - 5 \times 10^{-1} \text{M}$.

Section 12: Amperometric determination of Gold

This section deals with the new method of amperometric determination of Au(III) in the form of $\text{AuCl}_4^-$ ion in 0.5M NH$_3$ - NH$_4$Cl medium. Au(III) gives a cathodic wave in this medium with the limiting region starting from 0.0V. The electrode reaction probably involves reduction of Au(III) to Au(C). The wave, when subjected to titration with TSH at -0.6V results in L-shaped amperometric curve with the end point corresponding to Au(III) - TSH molar ratio of 1:1. Au(III) solutions in the concentration range of $5 \times 10^{-3} \text{M} - 6 \times 10^{-5} \text{M}$ have been estimated with maximum inaccuracy of 1%. The 1:1 ratio has been proposed to be due to the coordination of one TSH through its mercaptide group and one of the carboxylate groups.

PART II: TITRATIONS INVOLVING THIODIPROPIONIC ACID

Section 1: Amperometric determination of Manganese

This section deals with a new method of amperometric determination of Mn(VII) in the form of MnO$_4^-$ ion in 0.1M borax medium with the help of TDPS. A description of the two cathodic waves of MnO$_4^-$ in this medium has already been given. TDPS is not polarographically active. Both MnO$_4^-$
waves can be exploited for amperometric titration with TDPS solution. The titrations result in L-shaped curves which yield \( \text{MnO}_4^- - \text{TDPS} \) titrimetric molar ratio of 2:1. This ratio has been explained as follows:

\[
\begin{align*}
\text{TDPS} & \rightarrow \text{TDPS}^{2+} + 2e^- \quad \ldots \ (ix) \\
2\text{MnO}_4^- + 2e^- & \rightarrow 2\text{MnO}_4^{2-} \quad \ldots \ (x)
\end{align*}
\]

It is suspected that one of the \( \text{MnO}_4^{2-} \) ions formed enters into complexation with \( \text{TDPS}^{2+} \):

\[
\begin{align*}
\text{TDPS}^{2+} + 2\text{MnO}_4^{2-} & \rightarrow \text{MnO}_4^{2-} + \text{TDPS} = 0 - \text{MnO}_3 \quad \ldots \ (xi)
\end{align*}
\]

The other \( \text{MnO}_4^{2-} \) ion disproportionates to some extent to give the precipitate of \( \text{MnO}_2 \). The method yields good results in the \( \text{MnO}_4^- \) concentration range of \( 2 \times 10^{-3} \text{M} - 5 \times 10^{-5} \text{M} \).

**GENERAL SURVEY & DISCUSSION OF THE WORK**

This chapter deals with the general survey of the whole work described in various sections and an attempt to find out a correlation. The chapter starts with an account of the coordinating properties of the two ligands, TSH and TDPS and proceeds to classify the new titrimetric methods involving TSH into three categories on the basis of: (i) complexation of the metal species, (ii) oxidation of TSH by the metal species and (iii) compensation of the anodic current of TSH by the cathodic current of the metal species. Since TSH possesses soft as well as hard donor atoms, its reactions with various metal ions species studied have been discussed in the light of their such characteristics as well as other complexing
properties. The reaction of thiodipropionic acid, also containing hard and soft donor atoms, with MnO$_4^-$ ion has also been discussed on this very basis. Finally a comparison of complexing behaviour of the two ligand acids has been made. TSH enters into rather large scale coordination with various metal species while the complexing capability of TDPS is limited. This difference in behaviour has been explained on the basis of the difference in the nature of sulphur contained in the two acids. The effectiveness of TSH in this respect seems to be due to the easy deprotonation of $-\text{SH}$ group to result in the mercaptide group ($-\text{S}^-$) which plays a crucial role in determining its coordinating properties. As the sulphur of TDPS can never coordinate in this form and it is well established that the ability to coordinate falls in the order: $\text{S}^{2-} > \text{RS}^- > \text{R}_2\text{S}$, the above-mentioned difference in the complexing behaviour of the two ligand acids is explained.