CHAPTER I

Introduction to Voltammetry
Voltammetry is the term of electroanalytical chemistry that deals with the effect of the potential of an indicator electrode in an electrolysis cell on the current that flows through it. Voltammetry includes number of techniques such as d.c polarography, a.c polarography, cyclic voltammetry, chrono coulometry, chrono amperometry, pulse voltammetry, stripping voltammetry and differential pulse voltammetry. The current-voltage curves can be used for qualitative and quantitative determinations and also in the determination of thermodynamic and kinetic information about electrochemical systems. The indicator electrodes may be from any of a materials such as platinum, mercury, graphite, gold etc., and they may have almost any size, shape and construction and also may be stationary or in motion.

Polarography is a branch of voltammetry in which a dropping mercury electrode is used as the working electrode and a saturated calomel electrode as a reference electrode. In the present study the voltammetric techniques employed are d.c polarography and cyclic voltammetry.

In cyclic voltammetry, the potential applied between the indicator electrode and the reference electrode is varied with time in a triangular sweep mode. The forward or cathode potential sweep gives a reduction wave whereas the backward or anodic potential sweep gives an oxidation wave. This reduction-oxidation current potential curve is called a cyclic voltammogram.

D.C polarography has distinct advantages due to high sensitivity, low cost, easy measurement facilities and therefore suitable in the field of trace analysis.

Principles of polarography

The polarographic method of chemical analysis invented by Jaroslav Heyrovsky of Prague in 1920, is based on the unique characteristics of the current-voltage curves obtained when solutions of electro-oxidizable or electro-reducible substances are electrolyzed in a cell in which one is a micro electrode and the other a reference electrode. Current-voltage curves
are obtained by plotting the current obtained with the applied voltage to the micro electrode. The nature and concentration of electroactive substances present in the solution is identified from these current-voltage curves.

Many fields including Pharmaceutical Chemistry, Biochemistry and Environmental Chemistry utilizes this technique since it is the most sensitive analytical technique applicable to very small volumes of solutions. The proportionality between diffusion current and the concentration of the electroactive substances containing large excess of supporting electrolyte forms the basis of polarographic technique for the quantitative analysis of concentration range $1 \times 10^{-6}$ to $2 \times 10^{-3}$ M.

When the applied voltage and the current are recorded using a recording polarograph, an 'S' shaped graph will be obtained which is called a polarogram.

A typical current voltage curve is shown in fig. 1.1.

The working electrode, being polarisable, assumes the correspondingly increasing negative potential applied to it. From A to B, practically no current will pass through the cell. At B, the potential of the electrode is equal to the decomposition potential of the metal ion. The current present between A to B is called residual current. After the decomposition potential the current increases and the indicator electrode becomes depolarised by reduction of metal ion and the current rapidly increases flowing through the cell. At the point 'C' the current stops increasing linearly with applied potential but tends to a steady limiting value at the point 'D'. At the potential more negative than point 'D', the concentration of undischarged metal ion at the microelectrode surface is negligibly small relative to the metal ion concentration in the bulk of the solution. The increase in current from the residual current to the limiting current is called diffusion current, $i_d$, and is proportional to the concentration of the reducible substance in the solution. The potential at which the current is one half of the diffusion current is called half-wave
Fig. 1.1

Current (μA) vs. Applied E.M.F., V vs SCE

- Limiting current (C to D)
- Half-wave potential (B to C)
- Decomposition potential (A to B)
- Residual current (Line through A)

Key points:
- A: Residual current line
- B: Transition point
- C: Limiting current
- D: End of curve

Axes:
- Y-axis: Current (μA)
- X-axis: Applied E.M.F., V vs SCE

Values:
- Current range: 0 to 12 μA
- E.M.F. range: 0.6 to 1.6 V
potential, $E_w$. The half-wave potential of a reducible or oxidisable substance is independent of concentration and serves as a means of identifying the substances being reduced or oxidised. When several reducible substances are present in the same solution whose half-wave potentials are not identical, the nature of the substances can be established by a single run. The current-voltage curve for the reduction of several inorganic ions is shown in fig. 1.2.

Mercury is commonly used for micro electrode because of the following advantages.

1) Its surface is reproducible, smooth and continuously renewed; this is conductive to good reproducibility of the current-potential curve and eliminates passivity or poisoning effects.

2) Mercury forms amalgams with many metals.

3) The surface area can be calculated from the weight of the drops.

4) The use of mercury electrode is advantageous because of very high hydrogen over-voltage on this metal, to secure well defined waves for ions whose standard potentials lie far above that of hydrogen ion. It is thus electrode par excellence for the study of many electrode reactions.

Ilkovic examined various factors which govern the diffusion current and deduced the following equation.

$$i_d = 607 n D^{1/2} C m^{2/3} t^{1/6}$$

where

- $i_d$ = average diffusion current in micro amperes, $\mu A$.
- $n$ = number of electrons involved in the electrode reaction of one mole of species.
- $D$ = diffusion coefficient of electroactive material in $cm^2/sec$.
- $m$ = rate of flow of mercury, $mg/sec$.
- $t$ = drop time in seconds.
- $C$ = concentration of the electroactive material in mM / lit.
The terms \( m^{3/2} \) and \( t^{1/6} \) are dependent on the character and size of the capillary. The diffusion current depends on diffusion coefficient \( (D) \), the concentration of depolarising substance \( (C) \), number of faradays consumed in one mole of the electrode reaction and capillary characteristics of the electrode.

The validity of Ilkovic equation is decided by considering whether the polarographic wave obtained is diffusion controlled or not by considering the effect of following factors.

1) Concentration of electroactive substance

The diffusion current is directly proportional to the concentration of electroactive substance while other factors of the Ilkovic equation remain constant. Hence, a graph plotted between diffusion current and concentration of the substance should give a straight line passing through the origin if the wave is diffusion controlled. This forms the quantitative basis of polarography.

2) Mercury pressure

\( i_d \) is proportional to \( m^{3/2} t^{1/6} \), when the other factors in the Ilkovic equation are constant. ‘\( m \)’ is directly proportional and droptime, ‘\( t \)’ is inversely proportional to the pressure of the mercury on the capillary. The diffusion current is proportional to the square root of the pressure of mercury or \( i_d / \sqrt{h_{mg}} = K \). This method is applied to ascertain whether the height of the wave is diffusion controlled or not. If ‘\( K \)’ is not constant within the limits of experimental error over a wide range of mercury heights it may be concluded that the current must be either partly or wholly governed by the rate of some process other than the diffusion of metal ions.
Fig. 1.2

Applied E.M.F., V vs SCE

Current (μA)

-0.4  -0.8  -1.2  -1.6  -2.0

Mn^{++}

Co^{++}

Zn^{++}

Cd^{++}
3) **Temperature**

'D', the diffusion coefficient of the ion in the Ilkovic equation is given by the Nernst equation as

\[ D = RT \frac{\lambda^0}{zF^2} \]

Where

- \( R \) = gas constant
- \( T \) = absolute temperature
- \( \lambda^0 \) = Equivalent conductance at infinite dilution
- \( z \) = charge on the diffusing ion
- \( F \) = Number of coulombs per Faraday

The rate of diffusion and therefore the diffusion coefficient increases rapidly with rise in temperature. The diffusion current increases by about 1.3% for a one-degree rise in temperature. A large increase in the value is the common criteria for the kinetic (8-12%) or catalytic (3-10%) currents.

4) **Solvent composition and supporting electrolyte**

Since \( i_s \) depends on diffusion coefficient of the electroactive species which in turn depends on the viscosity of the solution, the increase in the viscosity causes \( i_s \) to decrease. If the species are spherical and larger than molecules of solvent, the Stokes-Einstein relationship predicts that \( i_s \) should be inversely proportional to the viscosity of the solution.

\[ i_s \propto \frac{1}{\eta^{1/2}} \]

\[ D = \frac{RT}{6\pi \eta r k} \]
where

\[ \eta = \text{viscosity of the solution} \]
\[ r = \text{radius of the diffusing particles} \]
\[ k = \text{Avagadro's number} \]

According to Stokes-Einstein relation, D should be inversely proportional to \( \eta \) and therefore \( i_s \) should also be inversely proportional to \( \eta^n \). Complexation of a metal ion decreases the diffusion current and shifts the half-wave potential to the more cathodic value in case of large size of the ligand compared to water molecule.

**Reversible and Irreversible processes**

At the dropping mercury electrode, the electrode reactions are divided into two classes, reversible and irreversible reactions. 'Reversible' reactions are those which are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the variations of current with potential, reflect the changing position of the equilibrium, which is described by the Nernst equation. The irreversible reactions are those which are slow that they proceed only a fraction of the way towards equilibrium during the life of each drop. Between these two electrode reactions there is an intermediate class of reactions that are fast enough to approach the equilibrium during the drop life but not so fast that they appear to reach it within the experimental error of the measurements. This type of electrode reactions are known as quasi-reversible reactions.

The value of standard rate constant, \( K \), of these reactions are given as follows:

1) Reversible process where \( K > 2 \times 10^{-2} \text{ cm/sec} \)
2) Irreversible process where \( K < 10^{-6} \text{ cm/sec} \)
3) Quasi-reversible process, \( K = 2 \times 10^{-2} \) to \( 10^{-6} \text{ cm/sec} \)
Maxima and Maximum suppressors

Current-voltage curves of a solution containing a reducible substance should be a smooth 'S' shaped curve, after applying correction for residual current. But many solutions give polarograms where the current increases much more rapidly and to a much higher value and decreases sharply approaching the plateau, as the potential becomes more negative. These maxima are observed most frequently at the beginning and occasionally in the middle of the straight portion of the limiting current.

Maxima of first and second kind are disadvantageous in all quantitative polarographic analysis. To measure the true diffusion current, the maxima must be eliminated and this can be done by the addition of very small quantity of surface active substances, such as gelatin, Triton X-100 etc.

Maxima is dependent on the nature and concentration of the material reduced or oxidised and also on the concentration of the indifferent electrolyte and the resistance of the circuit. In general the maxima become smaller, the longer the drop time of the electrode and increase with an increasing concentration of the electroactive material.

Gelatin is widely used as a maximum suppressor in analytical work and should be present in the solution in the range of 0.002 to 0.01%. The other equally important suppressor is Triton X-100 in the range of 0.002 to 0.004%. The effectiveness of a suppressor can be expressed as the maximum dilution or the minimum necessary for complete suppression of a given maximum.

Electrocapillary curves

Adsorption phenomenon can be undertaken by instantaneous current-time curves, pulse polarography, a.c polarography, electrocapillary curves and cyclic voltammetry.
The curve which expresses the relation between the potential of mercury and the surface tension at mercury solution interface is called the electrocapillary curve.

The potential on the electrode where it is uncharged is called the electrocapillary maximum potential or potential of zero charge. The electrocapillary maximum potential is dependent on the anions of the supporting electrolyte, for example in 0.1 M KCl solution the electrocapillary maximum potential is -0.461V vs SCE, while in 0.1 M KBr it is -0.535 V vs SCE and in 0.1 M KI it is -0.693 V vs SCE. The increasing negative value of electrocapillary maximum potential indicates the increasing strong adsorption of anion at DME.

**Effect of capillary active substances on electrocapillary curve are:**

1. At a given potential the surface tension is smaller in the presence of the capillary active substance than in its absence. Hence the maximum may not be shifted by the capillary active substances and the shape of the curve remains uncharged.

2. The adsorbed substances are dipoles oriented with the negative side to the mercury. The e.c. maximum shifts to more negative potentials. Many sulfur containing organic substances have such an effect.

3. If the adsorbed substances are dipoles oriented with the positive side to the mercury, the e.c. maximum is shifted to more positive potentials e.g., camphor and caffeine.

All curves coincide with the normal electrocapillary curve at negative potentials, indicating that the capillary active substances are desorbed at such potentials.
KINETIC, ADSORPTION AND CATALYTIC CURRENTS

Kinetic currents

Kinetic waves are those in which the height of a wave is partly or wholly determined by the rate of a chemical reaction that produces an electroactive substance in a thin layer of solution around the mercury drop.

The general mechanism responsible for kinetic waves may be given by the equation.

\[ \frac{K_f}{K_b} \]

\[ Y \xrightarrow{\text{forward}} O \]

\[ O + \text{ne} \xrightarrow{\text{back}} R \]

Where \( K_f \) and \( K_b \) are the first (or) pseudo-first-order rate constants for forward and backward reactions. The height of the kinetic wave depends on both the ratio of the equilibrium concentrations of \( Y \) and \( O \) in the bulk of the solution and the rate constants for their interconversion. It is convenient to begin by discussing the pure kinetic current that is obtained when the equilibrium concentration of \( O \) is negligibly small and when the transformation of \( Y \) into \( O \) is very slow.

Under these conditions the current is proportional to the rate of the transformation of \( Y \) into \( O \).

The current at any instant will be proportional to the area of the electrode at that instant, i.e., \( m \) and \( t \) as is given in the derivation.

\[ i_k = 493nD^{1/2}C_y m^{2/3} t^{2/3} \left( K_f/K_b^{1/2} \right) \]

where \( i_k \) = average kinetic current during the life of the drop, \( \mu_A \).

\( C_y \) = concentration of \( Y \) in the bulk of the solution, mM/L.

\( D \) = diffusion coefficient of \( Y \) or \( O \), cm²/sec

Since \( m^{2/3} \) \( i^{2/3} \) does not vary with the height of the column of mercury above the capillary, the height of a kinetic wave is independent of \( h_{mer} \) if all other conditions are kept constant.
There are other differences between kinetic and diffusion controlled waves. The height of a kinetic wave is larger than the diffusion current that would correspond to the equilibrium concentration of ‘O’ in the solution, but is smaller than the diffusion current that would correspond to the reduction of the O and Y together.

The disadvantage to use kinetic waves in practical analysis is that they afford poorer sensitivities than diffusion controlled waves and the impurities present in the solution may alter the height of a kinetic wave by catalysing the rate determining step.

Adsorption waves

Adsorption waves are those in which either the electroactive species or the product of the electrode reaction is adsorbed on the surface of the drop. In the electrode reaction:

\[ O + ne \rightarrow R \]

the product, R of the electrode reaction is adsorbed. Its activity is lower in the adsorbed state than in solution, and this facilitates the reduction of ‘O’. At very low concentration of ‘O’ there will be single wave, representing the reduction of ‘O’ to adsorbed R. Its height will be diffusion-controlled, proportional to the concentration of ‘O’ and also to \( h^{1/2}_{\text{corr}} \). But as the concentration of ‘O’ is increased, a point will be reached at which enough R is formed during the life of the drop to cover its entire surface. More than this amount of R can be formed only if the excess remains in the solution. Since it is more difficult to reduce ‘O’ to dissolved R than to reduce it to adsorbed R, the reduction of the excess ‘O’ will produce a second wave at a more negative potential. The first wave is the adsorption wave, whose height will be constant and independent of any further increase in the concentration of ‘O’ and second wave is the normal wave, which represents the reduction of ‘O’ to dissolved R. The reduction of all of the ‘O’ diffusing to the surface of the drop, and is diffusion-controlled and proportional to both the concentration of ‘O’ and \( h^{1/2}_{\text{corr}} \).
If 'O' is adsorbed and R is not, the single wave obtained at very low concentrations of 'O' will represent the reduction of adsorbed 'O'. On increasing the concentration of 'O', this wave will reach a limiting height when the amount of 'O' diffusion up to the surface of each drop is just sufficient to cover the drop surface. At a still higher concentration, the excess of 'O' remaining dissolved at the drop surface will produce a normal wave at a less positive potential.

In either of these cases the limiting height of the adsorption wave is proportional to the number of molecules adsorbed on the drop during its life. The total quantity of electricity corresponding to this number of molecules is given by

\[ Q = i_a t = 10^{22} n F A_{\text{max}} / a N \]

Where: 
- \( Q \) = number of microcoulombs flowing during the drop life.
- \( i_a \) = average current in micro amperes.
- \( A_{\text{max}} \) = maximum area of the drop, cm².
- \( a \) = area is \( A^2 \) covered by each adsorbed molecule.
- \( N \) = Avogadro's number.

The average current, \( i_a \), is given by the equation

\[ i_a = 13.66 \, \text{nm}^{2/3} \, t^{-1/3} / a \]

The limiting current of the adsorption wave is proportional to \( h_{\text{corr}} \).

This type of data on the limiting heights of waves have been used to calculate the areas of the molecule of certain organic mercury compounds which are adsorbed on the surface of a dropping electrode and also for the estimation of the atomic radius of arsenic.

Catalytic currents

Polarographic currents controlled by rate of reaction occurring at the surface of the electrode and in the vicinity of the electrode in addition to diffusion are called catalytic currents. Catalytic waves are very different in character from the usual diffusion controlled waves. They do not obey
Ilkovic equation, have either a very high or very low temperature coefficient and are not proportional to the height of the mercury column. There is a complicated relationship between limiting catalytic currents and $E_m$ of the catalytic wave on one hand and the concentration of the catalyst and the composition of the solution being analysed on the other.

Catalytic hydrogen waves can be observed at less negative potentials than the usual hydrogen discharge waves in the same solution. In contrast to the kinetic current, the limiting catalytic current can exceed the limiting current corresponds to the given catalyst concentration.

Later Herles and Vancura observed a wave different in its properties from diffusion currents in the polarography of blood serum in a supporting electrolyte of sodium salts in 1932. Heyrovsky and Brdicka observed catalytic waves of protein in the presence of cobalt(II) in ammoniacal buffer solution.

The catalytic process can be explained by considering an electrode reaction.

\[
\begin{align*}
O + ne & \rightarrow R \\
R + Z & \rightarrow O
\end{align*}
\]

Where $Z$, is not reducible at a certain potential if present alone, but causes the current obtained from the reduction of an electroactive substance, 'O' to increase by reacting with the product $R$ to regenerate 'O'.

The rate of the reaction is represented with the aid of the pseudo-first order rate constant $K_f C_f^0$, where $K_f$ is the second or pseudo-second-order rate constant and $C_f^0$ is the concentration of $Z$ at the surface of the electrode. If $K_f C_f^0$ is small, very little $R$ will be reoxidised, and the wave height will be equal to diffusion current of 'O'. But as $K_f C_f^0$ increases, the catalytic current becomes more important, and if $K_f C_f^0$ is very large,
the chemical reaction will produce more reducible material at the drop surface.

The average catalytic current over the life of a drop is given by

\[ i_c = 493 n D_{\text{eff}}^{1/2} C_0 m^{2/3} t^{1/3} \left[ (K_f + K_s) C_i^0 \right]^{1/2} \]

Catalytic currents can be identified by the fact that they do not vary with \( h_{\text{err}} \). There is proportionality between wave height and the concentration of the electroactive species ‘O’. The catalytic current is also proportional to the square root of the concentration of \( Z \) if \( C_0 \) and the composition of the supporting electrolyte are kept constant and if \( K_f, C_1 \) is sufficiently large. If \( (K_f + K_s) C_1 \) is not very large, the equation used is

\[ i_c / i_d = 0.812 \left[ (K_f + K_s) C_i^0 \right]^{1/2} + 1.92 \left[ (K_f + K_s) C_i^0 t \right]^{-7/8} \]

where \( i_d \) is the average diffusion current obtained during the drop life under certain conditions when \( Z \) is absent, while \( i_c \) is average current obtained under identical conditions but in the presence of \( Z \).

The catalytic currents fall into two categories. In the first type the limiting current of an electroactive substance is increased in the presence of a catalyst which itself is either polarographically inactive or reduced at considerably more negative potentials. Various catalytic waves of this type have been reported. Presence of hydrogen peroxide causes a large influence on the limiting current of ferric ion and few other known examples are of peroxy compounds of molybdenum, tungsten and vanadium.

1. \( \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} \)
   \( \text{Fe}^{3+} + H_2O_2 \rightarrow \text{Fe}^{2+} \)
2. \( V(V) \rightarrow V(IV) \)
   \( V(IV) + H_2O_2 \rightarrow V(V) \)
3. \( \text{Mo}^{VI} \rightarrow \text{Mo}^{V} \rightarrow \text{Mo}^{III} \)
   \( \text{Mo}^{III} + NO_3^- \rightarrow \text{Mo}^{V} \)
Mo(VI) gives a double wave, the first is due to reduction of Mo(VI) to Mo(V) and second is reduction of Mo(V) to Mo(III). The final product of simple electrode reaction Mo(III) reacts with nitrate in acidic solution to give back Mo(V). This Mo(V) is then reduced at the drop surface to give more Mo(III) which reacts with more nitrate and so on. The difference between the total height of the wave and the diffusion current obtained in the absence of nitrate is catalytic current of nitrate. These catalytic waves are obtained in many mixtures of transition metal ions with oxidizing agents like nitrate, hydrogen peroxide, chlorate, perchlorate and hydroxyl amine.

The second type of catalytic currents mostly seen with metal complexes are catalytic hydrogen waves. They are observed at less negative potentials than the usual waves of hydrogen discharge in the presence of metal complexes in the solutions of organic catalysts. The catalytic activity of organic catalysts is due to the presence of unpaired electrons and their ability to accept protons and form onium compounds. The catalytic waves are therefore observed in solutions of amines, sulfides, thiols, phosphines, oxonium compounds, arsines and sulfoxides. The presence of transition metal ions such as Co(II) and Ni(II) increases the catalytic activity of catalysts due to complexation.

The characteristics of catalytic hydrogen waves were first given by Brdicka using cobalt salt solutions in the presence of proteins. The effect of the catalyst concentration (C_{cat}) was determined and showed that with increasing C_{cat}, the limiting catalytic current increases first linearly with C_{cat}.

Then the increase of the wave height becomes slower. Finally, at high C_{cat} values, the limiting catalytic current becomes independent of C_{cat} and reaches a certain limit. He also found that the height of the catalytic wave and the limit that it can reach with increasing C_{cat} increases for higher buffer capacities of the solution and at lower pH. The dependence of the limiting current on the C_{cat} follows the form of the Langmuir
adsorption isotherm, if all other factors are held constant. This forms the basis of the theories of catalytic hydrogen waves.

Stromberg observed the growth of the catalytic wave caused by increasing protein and cobalt salt concentrations.

On the basis of all experimental data Brdicka and Stromberg proposed a scheme for catalytic hydrogen waves.

\[
\begin{align*}
B + HA & \rightleftharpoons BH^+ + A & (1) \\
BH^+ + e^- & \rightarrow BH & (2) \\
2HB & \rightarrow 2B + H_2 & (3)
\end{align*}
\]

B is a base in the solution, that is not reducible in the solution but can catalyze the reduction of protons. HA is a hydronium ion or another proton donor. As a result of electron transfer (2) a protonated form of the catalyst, unstable uncharged particle, is formed. The BH particles enter into a bimolecular interaction (3), regenerating the catalyst in the basic form. The basic form of the catalyst (B) is again protonated (1), discharged (2) and regenerated (3).

A great number of investigations have dealt with the catalytic waves in solutions of organic sulfur containing compounds, however several aspects of the mechanism of the process have not yet been fully clarified.

Shetty and Fernando\(^3\) examined the polarographic behaviour of bis-(O,O diethyl dithio phosphato) nickel(II) in ethanol-water medium at DME. Two waves are observed. The first wave is a catalytic wave which is due to complexed nickel(II) and the second wave is the reduction wave of nickel(II) that is not complexed by DTP. In the presence of an acid, a catalytic hydrogen wave also obtained in addition of these two waves, the polarographic wave of nickel(II) that is not complexed by DTP. The polarographic behaviour of Co(II) solution in the presence of thiols at HMDE in ammonia buffer shows adsorption property\(^4\).
Catalytic hydrogen waves produced by nickel in cysteine containing acetate buffer was examined by Banica and Calusaru⁶. The method was compared spectrophotometrically and found that nickel complexes with cysteine are involved in electrode reactions. The zero valent nickel complex formed during the catalytic nickel discharge acts as catalyst for hydrogen evolution and the two electrode processes are related closely. Galvez⁶ et al. suggested a mechanism for catalytic hydrogen wave obtained with dimethyl dithiocarbamate in the presence of Co(II) in ammonia buffer. Perez Ruiz and Martinez Moreno⁷ observed two catalytic hydrogen currents in the reduction process of 2,2-dithiobenzoic acid in the presence of Co(II) at DME.

Kolthoff and Mader⁸ studied the polarographic catalytic hydrogen waves of mercapto anilines in presence of Co(II) or (III) in acid or alkaline medium.

Catalytic hydrogen currents of low molecular weight thiols such as cysteine ethyl ester, cysteine, cysteamine, thiosalicylic acid, thioglycollic acid in buffers such as borax, phenol-sodium phenolate, tris-hydrochloric acid, ammonium chloride–ammonium hydroxide etc., in the presence of Co(II) ions exhibit typical kinetic characteristics and the rate-determining step is a chemical process⁹.

Proteins containing – SH or – SS – groups in an ammoniacal buffer in presence of Co(II) or Co(III) salts exhibit catalytic waves which are used to characterise the proteoharmones by mixing them in various proportions. Kuznetsov⁹ and Senda¹¹ et al. studied the nature of the polarographic protein waves in ammonia buffer containing hexamine cobalt chloride. They reported a theoretical equation for the Brdicka current produced by the protein in an ammoniacal buffer containing cobalt salt and explained the properties of the protein-cobalt(0) complex which catalyses the hydrogen evolution. They also showed that the catalytic activity of the protein-zero valence cobalt complex increases with the increase in temperature.
In the case of Brdicka currents, at less than 20% of saturation value the currents are kinetic in nature and at saturation value the current depends on metal ion concentration due to transport by diffusion of the metal complex to the mercury surface. A two-electron reduction of cobalt(II)-thiolate complex occurs at the electrode to form zerovalent cobalt-thiolate complex. This complex remains at the electrode and due to its increased basicity it reacts with protons which on further reduction liberates hydrogen.

\[
\begin{align*}
[\text{Co(II)}(\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z]_{\text{bulk}} & \xrightarrow{\text{diffusion}} [\text{Co(II)}(\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z]_{\text{e}} \quad (1) \\
[\text{Co(II)}(\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z]_{\text{e}} & \xrightarrow{2^\text{e}^-} [\text{Co}(0)(\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z]_{\text{e}} \quad (2) \\
[\text{Co}(0)(\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z]_{\text{e}} & \xrightarrow{\text{Protonation}} [\text{Co}(0)(\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z + \text{H}^+'_{\text{e}} + \text{B}] \quad (3) \\
[\text{Co}(0)(\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z]_{\text{e}} & \xrightarrow{\text{e}^-} [\text{Co}(0)(\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z]_{\text{e}} + \frac{1}{2} \text{H}_2 \quad (4)
\end{align*}
\]

[Co(II) (RS)_n (D)_y (H_2O)_z]_{e} at the electrode also must have been obtained by the following scheme from the thiol free species reaching the electrode surface which will follow the route 2, 3 & 4 mentioned above.

\[
\begin{align*}
[\text{Co(II)} (\text{D})_m (\text{H}_2\text{O})_n]_{\text{bulk}} & \xrightarrow{\text{diffusion}} [\text{Co(II)} (\text{D})_m (\text{H}_2\text{O})_n]_{\text{e}} \\
& \xrightarrow{\text{Complexation}} [\text{Co(II)} (\text{RS})_n (\text{D})_y (\text{H}_2\text{O})_z]_{\text{e}}
\end{align*}
\]

The subscript, zero refers to the vicinity of the electrode surface.

In the second type, the maximum 'A' is considered to be due to direct protonation of the cobalt(II) thiolate complex at the surface of the electrode and the protonated complex getting reduced to generate molecular hydrogen. The wave is of adsorption kinetic in character.
The origin of maximum 'B' in the second type of non-Brdicka current is stated to be from the decomposition of the cobalt(0) thiolate complex into thiol and cobalt(0) metal. The freshly deposited metallic cobalt liberates molecular hydrogen and thiol ion, $RS^-$ becomes RSH. The wave is surface-kinetic in character.

The direct discharge of hydronium ion on the stabilised atom of metallic cobalt on the surface of the mercury may also be from the thiol free species existing in solution before complexation.

Of these two mechanisms suggested for maximum 'B' the first one due to decomposition of complex to give Co(0) metal seems to be reasonable and requires further attention.
CYCLIC VOLTAMMETRY

Cyclic voltammetry is modern electrochemical technique which provides the means to examine the nature of an electrochemical reaction.

In this technique, the potential applied between the stationary working electrode (HMDE/SMDE) and the reference electrode (SCE) is varied with time in a triangular sweep mode. The cathodic or forward potential sweep gives a reduction wave, whereas anodic or backward potential sweep gives an oxidation wave. This complete reduction-oxidation current potential curve is called a cyclic voltammogram.

Matheson and Nichols\textsuperscript{12} established this technique and later developed by Sevcick\textsuperscript{13}. Well defined current potential curves for slow polarizations at stationary mercury electrode are given by Ceramak\textsuperscript{14}. A series of the papers by Shain and coworkers\textsuperscript{15-17} present a detailed theory of cyclic voltammetry. The utility of the technique was worked out by Randles\textsuperscript{18} for reversible processes and Delahay\textsuperscript{19} for irreversible processes.

The current-potential wave provides four measurable parameters, the net current at the peak of the cathodic response, the potential at peak of the cathodic response, the net current at the peak of anodic response and the potential at the peak of the anodic response.

The peak current of the forward potential scan for a reversible electrode reaction is

\[ i_p = 2.69 \times 10^3 n^{1/2} A D_0^{1/2} C_0 v^{1/2} \]

where

\[ i_p \quad \text{peak current, amperes/cm}^2 \]
\[ n \quad \text{number of electrons involved in the electrode process} \]
\[ A \quad \text{area of the electrode, cm}^2 \]
\[ D \quad \text{diffusion coefficient of the electroactive species in cm}^2/\text{sec} \]
Concentration, mole / cm³

scan rate of the applied linear voltage sweep, volts / sec

2.69 x 10⁶ = Randles - Sevcick constant.

An irreversible electrochemical reaction is one for which the charge transfer rate constant is small.

The peak current is given by

\[ i_p = 0.227 n F A C_0' K_s \exp \left( \frac{-\alpha n F}{RT} (E_p - E^0) \right) \]

A plot of log \( i_p \) vs \( E_p - E^0 \) of different scan rates yields, \( \alpha \) from the slope and \( K_s \) from the intercept, provided \( E^0 \) is known.

Shain and Nicholson calculated the peak potential for an irreversible response.

\[ E_p = E^0 - \frac{RT}{\alpha n F} \left[ 0.780 + \ln (D \alpha a)^{1/2} - \ln K_s \right] \]

There is a 30/α mV cathodic shift in peak potential for every 10-fold increase in scan rate, and this criterion can be used to characterize an irreversible response.

The shape of the peak of the irreversible response is independent of scan rate and the separation of \( E_p \) and \( E_{p/2} \) is given by

\[ E_p - E_{p/2} = \frac{-1.857 RT}{\alpha n F} \]

where \( E_p \) and \( E_{p/2} \) are the peak potential and half peak potential respectively.

Expression for quasi reversible cases are more complicated as it involves both diffusion and charge transfer kinetics and is given by Bauer.
The chemical reactions are of two types, chemical reaction following charge transfer and preceding charge transfer.

The parameters required to characterise the nature of these reactions are given below.

1) **Reversible chemical reaction following charge transfer**
   i) \( E_p \) shifts cathodically with an increase in \( v \) by an amount that approaches \( 60 / n \) per 10 fold increase in \( v \).
   ii) \( i_p / v^{1/2} \), current function is virtually constant with \( v \).
   iii) The anodic to cathodic current ratio \( i_p^+ / i_p^- \) decreases from unity as \( v \) increases.

2) **Irreversible chemical reaction following charge transfer**
   i) \( E_p \) shifts cathodically, by \( 30 / n \) mV for a 10-fold increase in \( v \).
   ii) \( i_p / v^{1/2} \) decreases with increase in scan rate.
   iii) There is no current on the reverse scan.

3) **Reversible chemical reaction preceding charge transfer**
   i) \( E_p \) shifts anodically with an increase in \( v \).
   ii) \( i_p / v^{1/2} \) decreases as \( v \) increases.
   iii) \( i_p^+ / i_p^- \) is greater than unity and increases as \( v \) increases with a value of unity approached at lower values of \( v \).

4) **Irreversible chemical reaction preceding charge transfer**
   i) \( E_p \) shifts cathodically by \( 30/n \) mV for a 10-fold increase in \( v \).
   ii) The current function \( i_p / v^n \) decreases with an increase in scan rate, \( v \).
   iii) There is no current on the reverse scan.

**Catalytic regeneration of reactant**

The catalytic mechanism refers to the case in which the product of an electrode reaction undergoes a homogeneous irreversible first-order or pseudo-first – order chemical reaction to regenerate the starting material.
The catalytic mechanism assuming the charge transfer is reversible has been treated theoretically by Saveant and Vianello\textsuperscript{21} and Nicholson and Shain\textsuperscript{16}. The diagnostic criteria for a catalytic reaction is as follows:

(i) \( E_p \) shifts anodically with an increase in \( v \) by an extent which goes through a maximum of 60/n mV per 10-fold increase in \( v \). No dependence of \( E_p \) on \( v \) is noted at either extreme in \( K/a \).

(ii) \( i_p / v^{1.2} \) increases at lower values of \( v \) and becomes independent of \( v \).

(iii) \( i_p^a / i_p^e \) is unity.

Adsortion - the cyclic voltammetric behaviour

Theory of cyclic voltammetry has been extended to study the adsorption phenomenon of electrochemical systems. The nature of the adsorption isotherm describes the process accurately.

The Langmuir isotherm is given by

\[
T = T' C / (K+C)
\]

where

\( T \) = Surface concentration
\( T' \) = Saturation value of the surface concentration
\( C \) = Solution concentration
\( K \) = proportionality constant

assuming that the adsorption – desorption processes to be sufficiently fast, the free energy of adsorption \( \Delta G \) is given by

\[
\Delta G = -RT \ln K
\]

The value of \( K \) is dependent on a number of experimental conditions like solvent, electrode surface, temperature etc.

The nature of the effects of adsorption processes on the cyclic voltammetric response has been treated by Wopschall and Shain\textsuperscript{22} and others\textsuperscript{23-25}.
Strong adsorption of the product of charge transfer

Processes involving strong adsorption of the product of charge transfer are frequently encountered in electrochemical reactions of organic compounds.

Under conditions in which both adsorption and diffusion control are significant, a response prior to the diffusion-controlled response is obtained for the reduction to the adsorbed state. The reverse potential scan also contains a response related to the adsorption process, which follows the diffusion controlled response. The separation in the peak potentials of the adsorption and diffusion controlled responses is a function of the free energy of adsorption. As the energy of adsorption increases, the separation in the peak potential of the two responses $\Delta E_p$ increases.

In case of strong adsorption of the product of charge transfer, the variation of the response with bulk concentration and scan rate is important. At very low concentrations the reduction to the adsorbed state is the primary process. As the concentration is increased, both processes are observed, and the relative height of the adsorption response to the diffusion controlled response decreases with an increase in concentration. The potential of the adsorption process becomes more anodic as the concentration increases by $60/n$ mV per 10-fold increase in concentration.

At very low values of the scan rate, the adsorption response may not appear. As the scan rate is increased, the adsorption response increases relative to the diffusion-controlled response. At very rapid scan rates, only the adsorption response is noted.

Strong adsorption of the reactant

In processes involving a strong adsorption of reactant are commonly encountered in electrochemical reactions of organic compounds. The relative magnitudes of the adsorption and diffusion responses are a function of concentration, with the adsorption response predominant at lower concentrations. As the bulk concentration is increased, the relative magnitude of the adsorption response decreases.
The variation of the relative magnitudes of the two responses with the rate of potential scan is again such that the diffusion process predominates at low scan rates and the adsorption process predominates at high scan rates.

Weak adsorption of the reactant

When the electroactive species is weakly adsorbed, the nature of the cyclic voltammetric response is different from strong adsorption. If the free energy of adsorption is low, the difference in potential between that required for reduction of the adsorbed reactant and that required for the soluble species is too small to show a separate response for the adsorbed material.

Variation in the response as a function of scan rate and concentration of reactant characterize the process.

Wopschall and Shain\textsuperscript{21} have presented theoretical calculation of this behaviour. A significant increase in the current function at faster scan rates is a strong indication of the presence of weak adsorption. As the concentration of reactant is increased, a greater portion of the total response occurs through diffusion control.

Weak adsorption of the product

The weak adsorption of the product is not as important as weak adsorption of reactant because this has little effect on the cathodic scan. With increase in scan rate, the cathodic peak shifts anodically and the peak height decreases. On the other hand, the anodic peak increases markedly with scan rate and becomes more symmetrical.

More complicated kinetic systems and/or more complex adsorption behaviour (both reactant and product adsorbed or product of electrochemical as well as chemical reaction adsorbed etc.) present difficult problems and such systems have not been studied in detail so far. The effects of an adsorption process on cyclic voltammetric data can only be observed and applied in the presence of coupled chemical reactions particularly with catalytic hydrogen currents of transition metal complexes of organic thio compounds.
CATALYTIC CURRENTS IN TRACE ANALYSIS

This is mainly responsible for the rapid and continuous progress in trace analysis, although the idea of trace or micro elements has been known for a long time in biological, agrotechnical, geological studies and forensic analysis.

As recognized recently, trace amounts of many metals and nonmetals are toxic if present in high concentration beyond tolerance limits.

Many analytical techniques are available for carrying out trace analysis namely, Atomic absorption spectroscopy, Neutron activation analysis, Fluorometry, Flame spectrometry, Anodic stripping voltammetry etc. Among all the analytical techniques, d.c. polarography is the most preferred technique for the trace element analysis because of following features. They are, (i) selectivity, (ii) high sensitivity, (iii) easy handling of equipment, (iv) low cost of equipment and (v) applicability for wide range of trace analysis. Polarographic technique involves the measurement of current at different voltage. Catalytic currents are most suited for trace level analysis of metal ions because of high sensitivity and selectivity. Selectivity can be greatly increased by variation of pH, reagent concentration, temperature, use of complexing agent, masking agent, separation techniques, activators, choice of suitable buffer etc. The complexing agents used are EDTA, diethyl amine etc., for the elimination of interfering ions for increasing the selectivity of catalytic reaction.

The selectivity of such monitoring systems is sufficient to allow the rate of the indicator reaction to be followed specifically enough to avoid complications from side reactions resulting from foreign ions.

Polarographic catalytic currents that have been used for the quantitative analysis of metal ions at trace levels have been reviewed here except those on Cr(VI), Fe(II), Co(II), Ni(II) and Cu(II). However, the
references on catalytic currents due to these ions have been included in the corresponding sections in the thesis.

Du and Huang\textsuperscript{26} reported a sensitive catalytic wave that was observed in acetate medium containing cadmium, bipyridyl, potassium iodide and iron(II). The method was applied to determine microamounts of cadmium in nickel base alloys and waste water.

The polarographic waves of copper (II) in the presence of sulphuric acid and thiourea was reported by Biernat and Syzmaszek\textsuperscript{27}. Copper was detected in aluminium alloys by Lei\textsuperscript{28} using sodium citrate buffer and benzoin oxime medium. An indirect polarographic method for the determination of Cu(II) based on the highly stable complex formation of Cu(II)-salicylaldehyde thiosemicarbazone was developed by Revathi and Palaniappan\textsuperscript{29}. The polarogram of Cu(II) in HCl-thioglycollic acid-1, 10-phenanthroline exhibits an adsorptive catalytic wave and was applied to determine trace amounts of copper in waste water and natural water\textsuperscript{30}.

Zhenan and Ying\textsuperscript{31} detected lead in waste waters without preconcentration in medium Vanadium(IV), NH\textsubscript{4}Cl-KI and NH\textsubscript{3}OH-HCl. Lingjuan\textsuperscript{32} determined lead in steel in HCl-ascorbic acid-sodium acetate-KI medium. The catalytic wave of lead and tin ammonium acetate-triethanolamine-cupferron medium was used for their detection by Yang and Zhang\textsuperscript{33}.

Wen\textsuperscript{34} reported catalytic currents of antimony(III) – ammonium oxalate-selenium(IV) system. Traces of antimony in soil, water, blood and mineral samples was analysed using catalytic wave of antimony-cupferron complex in HCl-sodium tartrate medium\textsuperscript{35}.

Wu et al.\textsuperscript{36} estimated trace amounts of antimony in tungstic oxide using polarographic catalytic waves with ferroin in the presence of sulphuric acid – ascorbic acid and sodium chloride solution. Chen and Zha\textsuperscript{37} observed a wave of antimony in dimethyl amino phenyl fluorone – sulphuric acid medium.
Arsenic (III) was detected in ores using catalytic polarographic wave in \( \text{H}_2\text{SO}_4-\text{Na}_2\text{SO}_4 \)-tartaric acid and KI medium\(^{48}\). According to Tao and Wu\(^{49}\) arsenic in biological samples can be estimated by catalytic polarography. Weide and Li\(^{50}\) identified traces of arsenic in minerals, rocks and samples of complex matrix using sulfate-O-phenanthroline hydrate-cobalt sulfate system.

Catalytic current method of tin(IV) in \( \text{H}_2\text{SO}_4-\text{HClO}_4-\text{NaBr-V(IV)} \) solution was applied to geological and biological samples by Gan et al.\(^{41}\). Tin was detected in trace amounts by its catalytic waves observed in triethylene tetra acetic acid (TTHA) in sulfuric acid medium at mercury electrode\(^{42}\). A catalytic polarographic method for the determination of microamounts of tin in iron and steel using \( \text{HClO}_4-(\text{NH}_3)_2\text{VO}_3-\text{KI-ascorbic acid system} \) was proposed by Xiao et al.\(^{43}\).

Uranium in ores was detected using its catalytic wave in acetic acid-ammonium acetate, EDTA, thionyl trifluoro acetone system\(^{44}\). Feng and Chen\(^{45}\) developed a catalytic polarographic method for uranium in acetic acid ammonium acetate-cupferron medium. Xiong and Wang\(^{46}\) reported the polarographic estimation of traces of silicon using 2-hydroxy-2-phenyl acetic acid and potassium chlorate in sulphuric acid. An indirect polarographic method for the determination of silicon in aqueous media was studied by Barrado et al.\(^{47}\) using the catalytic and kinetic reduction of \( \text{H}_2\text{O}_2 \) in the presence of Mo(VI) produced by the decomposition of 1,2-molybdo silicic acid.

Zirconium was determined in trace quantities because of its ability to form complexes with oxalic acid – cupferron- diphenyl guanidine adsorbable at dropping electrode and give catalytic currents\(^{48}\). Microgram quantities of zirconium(IV) has been analysed using catalytic reduction of iodate by the metal ion\(^{49}\). Gallium in the presence of alizarin was determined by Sommer and Umland\(^{50}\) using its catalytic waves.
A procedure for catalytic wave of iridium(III) with α-furil monooxime in acetate buffer and NaCl was developed by Ezerskaya et al. Kiseleva et al. developed a catalytic wave for Rhodium(III) in the presence of thiosemicarbazide and hydrochloride. Another method using thiosemicarbazide was given by Ezerskaya et al. Alexander reported trace analysis of serum proteins using the complex, trans-dichloro bis (N, N-dimethyl ethylene diamine) rhodium (III) chloride which is catalytically active at the dropping mercury electrode. The catalytic currents in solution of complexes of rhodium with organic ligands containing 'S' as functional groups were studied to improve the sensitivity of the determination of rhodium. The polarogram of rhodium-D, L-2, 3, 5, 6-tetrahydro-6-phenyl imidazothiazole chloride showed catalytic wave as per Zhou et al. Traces of rhodium(III) in tap and rinse waters of plating industry was detected applying the catalytic wave of Rh(III)-2-mercapto-benzothiazole complex in 1:1 DMF. Catalytic waves of ruthenium and rhodium in acetic acid medium using diethyl dithiocarbamate in DMF was observed by Medyantseva et al. Du et al. proposed the polarographic determination of indium with thioglycolic acid and 2,2'-bipyridyl in acetate buffer. Palladium(II) in presence of thiosemicarbazide gives catalytic hydrogen wave as per Rafi and Paul and using KSCN and NH₄I by Ma and Cai. Sun has estimated niobium(V) in ores using the system [2-5-(bromo-2-pyridylazo)-5-diethyl amino phenol] tartaric acid-sodium chlorate. Shen deduced a method for determining rhenium by catalytic polarography using H₂SO₄-EDTA-polyvinyl alcohol and diphenyl guanidine.

Molybdenum(VI) was estimated by Chikryzova et al. based on the catalytic waves obtained with organic compounds containing oxycarbonyl groups in acidic solutions. Ultra trace amounts of molybdenum in indium of high purity metals using the catalytic wave of nitrate ions was
determined by Bikbulatova and Sinyakova. Anisimova et al. studied the catalytic waves in solution of thiocyanates and thiosulfates in acetate and formate buffers with molybdenum (VI) compounds. A catalytic wave for molybdenum using a mixture of NaClO₄, mandelic acid and H₂SO₄ was developed by Henrion et al. Microgram amount of molybdenum (VI) was detected using the catalytic wave obtained with reacetophenone isoniazid hydrazone. Song et al. have analysed Mo(VI) using 4-2-pyridyl azoresorcinol in sulfuric acid medium in the presence of sodium chlorate. Barrado et al. estimated Mo(VI) at trace levels in the presence of salicylaldehyde and bromate in acetic acid-acetate medium.

Fe(III) and Co(III) with thiosemicarbazones of pyruvic acid and Benzoylformic acid give catalytic hydrogen waves, as described by Toropova et al. Zhengafi et al. reported simultaneous determination of nickel, copper, cadmium and cobalt in human hair and tea samples without interference with each other using catalytic hydrogen waves due to 1-(2-guindylazo)-2,7-dihydroxy naphthalene complexes.

Vanadium(V) has been determined by its catalytic wave in the presence of reacetophenone isonicotinic acid hydrazone and Bromate. Du and Song have deduced a method for determining vanadium by catalytic polarography using cupferron and 10% ammonium fluoride. Vanadium as V(IV) - ethylene diamine-N-hydroxyethyl-N,N,N-triacetate (HEDTA) in the presence of bromate was found to give catalytic wave by Zerebski. Trace levels of vanadium determination was established by Kuang using cinchonine and H₂SO₄ in acetate medium and a method for vanadium in ores. The catalytic wave of vanadium in 2-(3,5-Cl₂-2-pyridylazo)-5 dimethyl amino phenol - NaBrO₄-H₂SO₄ medium was applied for determination of vanadium in minerals and alloy steels.

A catalytic polarographic method for the determination of trace germanium in vegetables using the polarographic complex of Germanium (IV) pyrogallol - sodium bromate was developed by Shi et al.
Weng Shuahao et al. developed a method which is based on the catalytic effect of Fe\(^{3+}\) on the oxidation reaction between acid chrome blue and potassium bromate in sulphuric acid medium at 100°C and in 0.08 mol/L NH\(_4\)OH - 0.01 mol/L (NH\(_4\))\(_2\)SO\(_4\) supporting electrolyte. This method was applied in the determination of iron in natural water and food materials with satisfactory results.

Xiaobo et al. determined Se in human hair by catalytic polarography and the results were compared with fluorescence spectrophotometry. Maslowska developed a voltammetric method for the determination of trace metal ions in foods. Xiangchun et al. described a new polarographic adsorptive catalytic wave for the determination of trace Te in smog dust and wheat floor. The detection limit was 2x10\(^{-4}\) g/ml.

Mingzhang et al. developed a method for the determination of cadmium in mouse kidney by catalytic polarography and the results were consistent with those of AAS and the detection limit was 0.005 \(\mu\)g/mL. A method for the direct and rapid determination of trace titanium in iron and steel by catalytic polarography was proposed by Guiyou et al. without any separation with the relative standard deviation of 2.9-5.8%. Molybdenum in human hair was determined by catalytic polarography in a base solution containing sulphuric acid 0.032 M, Na\(_2\)SO\(_4\)0.11M, hydroxyl phenyl acetic acid 0.048 M and NaClO\(_3\) 0.63M.

A method for the direct rapid determination of micro molybdenum in steel by catalytic polarography was developed and used in the determination of molybdenum in standard alloy samples by Guiyou et al. Vrublevs and Tymoshuk reported the mechanism of onset of polarographic catalytic hydrogen currents in solution of ruthenium.

Polarographic determination of total iron content using a Fe\(^{2+}/^{3+}\) - methylthymol blue- NO\(_3\); system was described by Yang and Wang.

Polarographic catalytic currents that have been used for the quantitative analysis of metal ions at trace levels have been reviewed here.
except those on Fe(II), Co(II), Ni(II), Cu(II) and Cr(VI). The references on catalytic currents due to these ions have been included in the corresponding sections in the thesis.

Polarographic catalytic hydrogen waves caused by the presence of organic ligands containing –SH groups provide one of the most sensitive analytical methods for the determination of trace and ultra-trace quantities of many transition metal ions in ores and alloys, environmental, biological, agricultural and pharmaceutical samples.
AIM OF THE WORK

A remarkable growth has been found in technological and industrial activity in the last few decades. The environmental pollution also increased to a large extent. With the advancements in technology a great number of new processes, methods and products have been introduced. The combination of new pollutants results in compounds of undefined character, hence growth and complexity of environmental pollution increases.

The introduction of the pollutants into the environment in significant amounts is in the form of sewage waste, accidental discharge, by product of the manufacturing processes or other human activity. Water (drinking water, domestic water and agricultural water), soil and agricultural materials and air are naturally influenced by the various pollutants at all levels.

The Bhopal disaster, lead poisoning at Talasari, mercury poisoning at Shadnagar are few environmental issues in India among many making the survival of living species a challenge.

A special characteristic property of heavy metals is their strong attraction to biological tissues. Most of the metals are essential but beyond their tolerance limits are harmful to the living systems as they are capable of reacting with binding sites of the biological tissues resulting "protein precipitation" and in the formation of metal complexes with sulphhydril groups, amino, phosphato, carboxylato groups and hydroxyl radicals of enzymes and biological proteins. The analysis of pollutants is therefore highly essential to assess their levels inorder to characterise them for clinical diagnosis, treatment of their effects and for suggesting a control mechanism etc.

A perusal of the literature also indicates a great interest on catalytic hydrogen currents at DME due to cobalt and nickel complexation with proteins. Since proteins have –SH groups as the binding site, simple
xanthates with the same binding site have been selected to study the catalytic activity at DME for few metal ions. Potassium heptyl xanthate and potassium iso-octyl xanthates are not only simple but also found to be advantageous because of the formation of the soluble complexes with a number of metal ions, facilitating the polarographic technique more sensitive through catalytic hydrogen currents under suitable experimental conditions.

Iron is primary constituent of haemoglobin and most of the human disorders and diseases are due to blood or through the blood. Water is the main source to procure all the essential constituents of the body and there is every chance even to secrete the essential constituents in toxic levels.

Similarly chromium is also having essential and toxic role in humans. As it is widely used in various fields particularly in leather industry, its analysis in industrial effluents and surrounding environmental water samples has significant importance.

Hence, it is found worthwhile to develop simple and rapid methods for nickel, cobalt, iron, copper and chromium using xanthates by catalytic polarography and to apply the method for the analysis of various water samples, agricultural materials and pharmaceuticals. An attempt has been made to suggest a mechanism to fit into the already reported ones with nickel, cobalt, iron and copper along with the supported evidence by cyclic voltammetric results.
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