CHAPTER I

Introduction to Voltammetry
Voltammetry is the term used to designate measurement of current-voltage curves obtained at a micro electrode. 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. Voltammetry includes a number of electrochemical techniques such as d.c polarography, cyclic voltammetry, a.c polarography, chronocoulometry, chronoamperometry, oscillo polarography, pulse voltammetry etc.

The basic principles of electrochemical techniques such as d.c polarography and cyclic voltammetry that are used in the present study have been discussed in this chapter briefly.

D.C Polarography

Polarography is the branch of voltammetry which is associated with the Heyrovsky and Shikata of which, the Nobel prize Winner Heyrovsky introduced the technique and Shikata helped in the construction of the cell. Kolthoff and Laitinen advocated a more descriptive general name 'voltammetry' to indicate that the voltage and current are the two quantities measured. The importance of this technique lies in the uniqueness of obtaining current-voltage curves, when solutions of electro-oxidizable or reducible substances are electrolyzed in a cell, is which one electrode consists of mercury falling drop wise from a fine bore glass capillary and is polarised to different potentials, by voltage applied from an outside source between it and a reference electrode.
The method consists of measurement of the current as a function of applied voltage. As the potential increases, the current obtained due to the electron transfer to the electroactive species attains a maximum value called limiting current which shows that the net concentration of the electroactive species on the surface of the electrode is zero. The depolariser is a dilute solution of the compound under investigation taken in a suitable medium containing an excess of indifferent electrolyte whose concentration is normally fifty fold to that of the electroactive species.

By applying steadily increasing voltage to the polarographic cell, a reproducible current-potential pattern can be obtained. When the e.m.f is applied to the cell, the species capable of involving in electron transfer reaches the electrode surface by a process called mass transfer. Mass transfer takes place by means of three factors, migration, diffusion and convection. Out of the three modes of mass transport, convection is minimised by avoiding stirring while electrical migration is suppressed by the addition of large excess of an inert electrolyte (i.e., supporting electrolyte) and hence diffusion becomes the only significant transport process under polarographic conditions. The limiting current is therefore designated as diffusion current. Theoretical considerations require the use of a polarizable electrode with small surface area and a large unpolarizable reference electrode. Dropping mercury electrode in which reproducible droplets of mercury fall at a constant rate from a capillary tube (with an approximate internal diameter of 0.06 - 0.08 mm) is used as polarizable electrode.
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 (Fig. 1).

The potential corresponding to the mid point of the polarogram is referred to as the half-wave potential \((E_{\text{w}})\) which is generally independent of concentration but characteristic of the depolariser.

It can be seen from the Fig. 1 that from A to B a small current flows. This is known as residual current and is carried by the supporting electrolyte and impurities present in the sample. At point B, the potential of the electrode becomes equal to the decomposition potential of reducible or oxidizable ions present in the solution.

The current then increases along the curve BC. At point C current no longer increases linearly with applied voltage but reaches a steady limiting value at point D. Thus the current corresponding to the curve CD is known as limiting current. The difference between the residual current and the limiting current is called diffusion current and is generally denoted by \(i_d\). Its magnitude is proportional to the concentration of the reducible substance in solution. The magnitude of the diffusion current on the other hand, is a measure of the quantity of the substance present in the solution, so that a polarographic curve serves to identify an ion qualitatively and quantitatively. When several reducible substances are present in the same solution and the respective half-wave potentials are not too close to one another, the nature and quantities of the substances can be established by a single run. The polarographic curve in such a case
Fig. 1: Typical current - voltage curve obtained with the droping mercury electrode
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contains a series of diffusion current curves which are produced as the voltage is gradually increased and the substances are reduced or oxidized inorder, based on their decomposition potentials in that medium. The general appearance of such a curve for the reduction of several inorganic ions is shown in Fig.2.

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

1. It provides a continually renewed electrode of a very pure metal not affected by any previous electrolysis or aging process and with a perfectly reproducible, fresh surfaces.

2. During the reduction of many metabolic ions, the deposited metal does not accumulate on its surface but diffuses into the body of the mercury drop as an amalgam.

3. The dropping mercury electrode is a micro electrode. Hence, the electrolytic currents remain small, leaving the composition of the test solution unaltered. This permits repeated polarographic analysis of the same solution with identical results.

4. By changing the pressure head on a given capillary, the rate of growth of mercury drop and its surface can be altered without changing the final size of the drop. The resulting changes in the observed current gives clues to the mechanism of the electrode reactions.

5. The largest hydrogen over voltage is found on mercury. This means that the potential at which hydrogen ions are reduced at a mercury electrode is far more negative than at any other electrode. Hence
Fig. 2: Polarogram of a solution containing several metal ions in presence of large excess of indifferent electrolyte and 0.01 per cent Gelatin
the d.m.e. is suitable for analysis in acid solutions and in regions of more negative potentials than electrodes of other metals. It is thus the electrode par excellence for the study of many electrode reactions.

An important mathematical relationship pertaining to the diffusion current at any time during the drop life is given by Ilkovic\textsuperscript{4} as:

\[ i_d = 607 n D^{1/2} m^{1/6} t^{1/6} C \]

where

\begin{align*}
  i_d &= \text{average diffusion current in micro amperes, } \mu\text{A} (10^{-6} \text{ amp}) \\
  n &= \text{number of electrons involved in the electrode reaction} \\
  C &= \text{concentration of the electroactive material in mM/litre} \\
  D &= \text{Diffusion coefficient of electroactive material in cm}^2/\text{sec} \\
  m &= \text{rate of flow of mercury through column, mg/sec} \\
  t &= \text{time between two successive drops of mercury, sec.}
\end{align*}

The terms \( m^{2/3} \) and \( t^{1/6} \) are dependent on the character and size of the capillary and the terms \( n, C \) and \( D^{1/2} \) are determined by the properties of the solute and solution.

Sometimes the factors pertaining to any one electrode process under a fixed set of experimental conditions are combined in a single factor \( I \), called the diffusion current constant given as

\[ I = 607 n D^{1/2} \frac{i_d}{C m^{1/3} t^{1/6}} \]

The diffusion current is dependent on number of factors including the diffusion coefficient of the depolarising substance and its concentration in the body of the solution, number of faradays consumed in one mole of the electrode reaction, the area of the electrode and the transfer coefficient.
The Ilkovic equation is valid only if the wave obtained is solely due to diffusion of ions from the body of the solution to the electrode surface. This equation fails, if the wave obtained is partly or wholly controlled by the kinetics of the reaction due to the presence of catalytically active substances in solution or the adsorption of either the oxidized or reduced ions or groups on the surface of mercury drop.

The validity of this equation is decided by considering whether the polarographic wave obtained is diffusion controlled or not. Diffusion current is affected by a number of factors such as concentration of the electroactive substance, mercury pressure, temperature and solvent composition and supporting electrolyte.

1) Concentration of the electroactive substance

When all the other factors in the Ilkovic equation remain constant, the diffusion current \( (i_d) \) is directly proportional to the concentration of the reducible or oxidizable substances. Hence a graph plotted between the diffusion current and concentration of the substance should give a straight line if the wave is diffusion controlled. This forms the quantitative aspect of polarography.

2) Mercury pressure

It may be stated that \( i_d \) is proportional to \( m^{2/3} t^{1/6} \) when the other factors in the Ilkovic equation are constant. The drop time \( t \) depends upon the height of the mercury column. The proportionality constant 'k' between the limiting current and the square root of the height of the mercury column should be constant; \( k = i_d / \sqrt{h} \) if the wave is diffusion controlled.
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This is the basis of a simple and frequently used method of ascertaining whether the height of wave is diffusion controlled or not. If 'K' is not constant within the limits of experimental error over a wide range of the heights of mercury column it may be concluded that the current must either be partly or wholly governed by the rate of some process other than the diffusion of metal ions.

3) Temperature

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

\[ D = \frac{RT}{ZF^2} \times \lambda_s \]

Where
- \( R \) = gas constant in volt-coulombs per degree
- \( T \) = absolute temperature
- \( \lambda_s \) = equivalent conductivity at infinite dilution
- \( Z \) = charge of the ion
- \( F \) = number of coulombs per Faraday

The conductivity of the solution varies rapidly with temperature. With the variation of conductivity there is a corresponding change in 'D' and hence in \( i_d \). In normal cases 'D' and \( i_d \) values increase by 2-3% per degree rise in temperature. A large deviations from these values are common criteria for kinetic and catalytic currents.

4) Solvent composition and supporting electrolyte

The diffusion current, \( i_d \) depends on the diffusion coefficient of the electroactive species which inturn depends on the viscosity of the solution. The increase in the viscosity causes \( i_d \) to decrease. If the electroactive
species are spherical and much larger than the molecules of the solvent, the
diffusion coefficient may be given by Stokes-Einstein relation

\[ D = \frac{R T}{6 \pi \eta r^4} \]

Where \( \eta \) = viscosity
\( r \) = radius of the diffusing particles
\( k \) = Avagadro's number

According to Stokes-Einstein relation, \( D \) should be inversely proportional to \( \eta \) and therefore \( i_d \) should also be inversely proportional to \( \eta^{-4} \). 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

Electrode reactions at the dropping mercury electrode are divided into two extreme classes. One is reversible and the other is irreversible reactions. Reversible reactions are so rapid that the thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. On the other hand irreversible reactions are so slow that they proceed only a fraction of the way towards equilibrium during the life of each drop. For these reactions it is the rate of the electron-transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between the current and potential. Between
these two electrode reactions there is an intermediate class of reactions that are fast enough to approach equilibrium during the drop life but not quite so fast 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, $K_s$, of these types of reactions are given as follows.

1. Reversible process, $K_s > 2 \times 10^{-2} \text{ cm/sec}$
2. Irreversible process, $K_s < 10^{-6} \text{ cm/sec}$
3. Quasi-reversible process, $K_s = 2 \times 10^{-2}$ to $10^{-5} \text{ cm/sec}$

The following points are considered to decide whether the electrode reaction is reversible or not.

1. The potential of the dropping mercury electrode at any point on the polarogram, provided the electrode reaction is a reversible one, is given by Heyrovsky and Ilkovic as

$$E_{d.m.e} - E_n = \frac{0.0591}{n} \log \frac{i}{i_d}$$

Where $i = \text{current}$

$$E_{d.m.e} = \text{applied potential}$$

The above equation states that if the electrode reaction is reversible, the slope of the plot of $E_{d.m.e}$ versus $\log i/i_d - i$ is $-0.0591/n$ volts and the potential at which the log term is equal to zero is the half-wave potential of the polarogram. No systematic divergence of the points from the straight line may be found over a wide range of the long term from at least -1.5 to +1.5. It is possible that the experimental errors may combine in such
a way that the observed slope of such a plot for reversible wave may differ from the theoretical value by 3-5 mV but any difference greater than this is a proof of irreversibility.

2. A much more simple, rapid and convenient method suggested by Tomes requires the measurement of $E_{w}$ and $E_{v}$. These are the potentials at which the current is equal to three fourths and one fourth of the diffusion current. At $E_{w}$, we have

$$
E_{w} - E_{v} = \frac{0.0591}{n} \log \frac{i_{d}}{i_{d}/4}
$$

and at $E_{v}$

$$
E_{v} - E_{w} = \frac{0.0591}{n} \log \frac{1}{3}
$$

so that

$$
E_{w} - E_{v} = \frac{0.0591}{n} \log 3
$$

consequently the value of $E_{w} - E_{v}$ for a reversible electrode reaction should be equal to $-0.0564/n$.

3) The half-wave potential of a reversible wave is independent of the concentration of the substance being reduced or oxidized. An appreciable variation of $E_{w}$ with concentration is a proof of irreversibility of the reaction. The reverse is not true, however, for the half-wave potential of many irreversible waves are also independent of concentration.
4) The most conclusive proof of reversibility of a reaction is secured when polarograms of solutions containing the reduced form of redox couple involved in the reaction are found to give anodic waves whose half-wave potentials are identical with the cathodic half-wave potentials of the oxidised form. This is the same thing as securing a composite wave with no inflection around the residual current curve with a solution containing both the oxidized and the reduced forms. It is worth while to make sure that the cathodic and anodic diffusion currents obtained with equal concentrations of the reduced and oxidized species are approximately equal. In such a case the point of inflection is the redox potential of the system.

5) In a polarographic double wave if the electrode requires the same number of electrons the slope of the two waves and their id's must be equal, if the wave obtained is reversible.

6) The temperature coefficients of a reversible wave depends on the nature of the electrode reaction. For a reduction to a metal soluble in mercury, \( \frac{dE}{dt} \) is about -0.7 mV/degree and for a homogeneous reduction \( \frac{dE}{dt} \) may be either positive or negative but is rarely greater than +1 mV/degree. The temperature coefficients of \( E_t \) for an irreversible wave is almost positive and is usually of the order of several mV/degree. Larger temperature coefficients of \( E_t \) therefore constitute a fair evidence against the reversibility of the wave.
Maxima and maximum suppressors

The most undesirable phenomena that is usually encountered in quantitative polarographic analysis is the appearance of a maximum. A polarogram after proper correction for the residual current should be a smooth 'S' shaped curve perfectly symmetrical about the half-wave potential, reaching the plateau from below. In the absence of any maximum suppressors, usually the current increases very rapidly and to a higher value than expected, then decreases sharply and reaches the plateau from above as the applied potential becomes more negative. This is perfectly reproducible.

Heyrovsky classified maxima into two classes, a positive and a negative maxima according to whether it occurs on the positive or negative side of the electrocapillary maximum potential.

No theory advanced so far is sufficient to explain the occurrence of maxima. Heyrovsky is of opinion that electroreducible or oxidizable substances are adsorbed on the mercury drop, whereby the concentration of the reducible substance is increased above its value in the body of the solution, which results in a maxima.

Maxima of first and second kind are disadvantageous in all quantitative polarographic analysis. To measure the true diffusion current, the maxima must be eliminated by adding surface active materials called as maximum suppressors such as gelatin, triton X-100, methyl red, etc.

The maximum suppressors most widely used are gelatin and triton X-100. Triton X-100 is a stable compound and can be used for years. The
effectiveness of a suppressor can be expressed as the maximum dilution or the minimum necessary for complete suppression of a given maximum. Gelatin is used as a maximum suppressor and should be present in the solution in the range of 0.002 to 0.01%, whereas triton X-100 in the range of 0.002-0.005%.

**Electrocapillary curves**

The curve which expresses the relation between the potential of the mercury electrode and the surface tension at a mercury solution interface is called the electrocapillary curve.

The adsorption phenomenon can be studied by using electrocapillary curves, current-time curves, a.c. polarography, pure polarography and cyclic voltammetry. These waves are measured in the solution of a supporting electrolyte and in the presence of a surface active compound.

On the basis of electrocapillary curves measured at several concentrations of the surface-active compound, the quantities of adsorbed compound can be calculated. The surface tension of cathodically polarised mercury first increases and then decreases with increasing negative potential according to Lippmann.

The potential on the electrode where it is uncharged is called the electrocapillary maximum potential and is dependent on the anions of the supporting electrolyte, for example in 0.1 M KCl solution the electrocapillary maximum potential is -0.461 V 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

a) The surface tension at a given potential is smaller in the presence of the capillary active substance than its absence. Hence the maximum may not be shifted by the capillary-active substances and the shape of the curve remains unchanged.

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

c) The adsorbed substances are dipoles oriented with the positive side to the mercury. The electrocapillary maximum is shifted to more positive potentials. Eg: Caffeine and Camphor.

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

Polarographic limiting currents which are influenced by the kinetics of preceding coupled chemical reactions are known as kinetic currents.

Kinetic wave is an important stage in the development of polarography. In kinetic waves the transport of electrochemically active materials to and from the electrode is determined not only by diffusion but also by the chemical reaction taking place at the electrode surface.
Kinetic currents are different from diffusion currents which can be explained by taking an equation

\[
\begin{array}{c}
C \xrightarrow{\rho} A \xrightarrow{\rho \sigma} B
\end{array}
\]

The equilibrium between these forms in the solution is given by the corresponding constant.

\[
\sigma = \frac{[C]}{[A]}
\]

and the rate of attainment of equilibrium depends on the ratio of the rate constants of the forward (\(\rho\)) and reverse (\(\rho \sigma\)) reactions.

To develop the quantitative relationships controlling kinetic currents, the simple method of Brdicka and Wiesner\(^7\) and Wiesner\(^8\), is based on the concept of reaction layer, can be used. If compound A is used in the electrochemical reaction, the equilibrium \(C \rightleftharpoons A\) is shifted almost completely at the surface of the electrode, and the degree of shift decreases with the distance from the electrode towards the bulk of the solution. The layer in which the shift of equilibrium takes place is called the reaction layer.

The kinetic current is determined by the number of electrochemically active particles formed within the reaction layer in unit time. If the thickness of the reaction layer is taken as \(\mu\), then the volume of the layer will be \(\mu a\) and the limiting kinetic current can be given by
\[ i_{\text{lim}} = nF \mu_s \rho C_s \]

\[ \mu_s = \text{average surface area of the dropping electrode during the life of the drop} \]

\[ C_s = \text{Concentration of the electrochemically inactive compound C in the reaction layer.} \]

The concentration, \( C_s \), depends on the rate of the \( C \cdot A \) reaction. If the rate of this reaction increases, the value of \( C_s \) decreases and the limiting current becomes zero. Under these conditions, the kinetic current will be determined by the diffusion of compound \( C \) from the bulk of the solution and that it will attain the value of the diffusion current, \( i_d \), for compound \( C \) as per Ilkovic equation as

\[ i_d = X C_0 \]

The concentration \( C_s \) can be expressed by

\[ C_s \cdot \frac{i_d}{i_{\text{lim}}}X \quad (X = \text{proportionality constant}) \]

substituting the value of \( C_s \) in the above equation

\[ \frac{n_s \cdot F \mu \rho / X}{1 \cdot n_s \cdot F \mu \rho / X} = \frac{i_d}{i_{\text{lim}}}X \]

The thickness of the reaction layer \( \mu \) can be determined by the equation

\[ \mu = \sqrt{\frac{D}{\rho \alpha}} \]
If the thickness of the reaction layer is small \([C]_s = [C]_e\), the value

\[
[C]_s = C_s
\]

The basic characteristic of a completely kinetic current value is independent of the height of the mercury column, \(h_{\text{Hg}}\). The average surface of the dropping electrode during the life of the drop is

\[
s = \frac{3}{5} \times 0.85 \ m^\frac{1}{5} \ t^\frac{1}{5}
\]

The second characteristic property of kinetic current is its high temperature coefficient value.

**Adsorption waves**

Adsorption waves\(^9\)\(^1\)\(^0\) 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 a very low concentration of ‘O’ there will be a 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 \(h_{\text{corr}}^\frac{1}{2}\). 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, 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 original wave is the adsorption wave, whose height will be constant and independent of any further increase in the concentration of 'O'; the second wave is the normal wave, which represents the reduction of 'O' to dissolved 'R'. The total height of the double wave corresponds to the reduction of all of the 'O' diffusing to the surface of the drop, and is therefore diffusion controlled and proportional to both the concentration of 'O' and $h_{corr}^{\frac{1}{2}}$.

If 'O' is adsorbed and 'R' is not, the single wave obtained at very low concentration 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', diffusing 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
\[ Q = i_a t = 10^{22} n F A_{\text{max}}/aN \]

where

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

The factor \( 10^{22} \) permits \( i_a \) to be expressed in \( \mu \)amp.

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

\[ i_a = 13.66 \, nm^{1/5} \, t^{1/3} \, a \]

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 molecules 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 the 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 currents are very different in character from the usual diffusion controlled waves. They do not obey Ilkovic equation, have either
a very high or a very low temperature coefficient and are not proportional to the height of the mercury column.

Catalytic currents are two types. In the first type, the limiting current of the electroactive substance is increased in the presence of a catalyst which itself is either polarographically inactive or reduced at considerably more negative potentials. Examples of this type are the reduction at Fe(III), Mo(VI), Ti(IV), V(V) in the presence of oxidizing agents such as hydrogen peroxide, chlorate, perchlorate, nitrate, hydroxyl amine etc. which act as catalysts.

![Diagram of catalytic currents](image)

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 to formonium compounds. The catalytic waves are
therefore observed in solutions of amines, thiols, sulfides, phosphines, arsines, oxonium compounds and sulfoxides. The presence of transition metal ions such as Co(II) and Ni(II) increases the catalytic activity of the catalysts due to complexation.

The characteristics of catalytic hydrogen waves were first given by Brdicka\textsuperscript{11} using cobalt salt solutions in the presence of proteins. With increase in the catalyst concentration ($C_{\text{cat}}$) the limiting catalytic current first increases linearly with $C_{\text{cat}}$, then the increase of the wave height becomes slower. At high $C_{\text{cat}}$ values, the limiting catalytic current becomes independent of $C_{\text{cat}}$ and reaches a certain limit. He also found that the height of the catalytic wave and the limit that it can reach with increasing $C_{\text{cat}}$ increases for higher buffer capacities of solution at lower pH. The dependence of the limiting current on the $C_{\text{cat}}$ follows the form of the Langmuir adsorption isotherm, if all other factors are 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^- \quad (i) \\
BH^+ + e^- & \rightarrow HB \quad (ii) \\
2HB & \rightarrow H_2 + 2B \quad (iii)
\end{align*}
The process occurs in solutions containing a base $B$ that is not reducible but can catalyse the reduction of protons. HA is a hydronium ion or another proton donor. As a result of electron transfer (ii) to the protonated form of the catalyst, an unstable uncharge particle is formed. The HB particles enter into a bimolecular interaction (iii). Organic sulfur containing compounds have catalytic property and this property is enhanced by transition metal ions, regenerating the catalyst base and liberating molecular hydrogen. The catalyst is again protonated by step (i), discharged by step (ii) and regenerated by step (iii).

Shetty and Fernando$^{12}$ examined the polarographic behaviour of bis-(0,0 diethyl dithio phosphate) 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$^{13}$.

Banica and Calusaru$^{14}$ examined the catalytic hydrogen waves produced by nickel on complexation with cysteine in acetate buffer. Galvez et al.$^{15}$ suggested a mechanism for catalytic hydrogen wave obtained with dimethyl dithiocarbamate in the presence of Co(II) in ammonia buffer. Perez
Ruiz and Martinez Moreno \(^{16}\) observed two catalytic hydrogen currents in the reaction process of 2,2-dithiobenzoic acid in the presence of Co(II) at DME.

The polarographic catalytic hydrogen waves of mercapto anilines in presence of Co(II) or (III) in acid or alkaline medium were studied by Kolthoff and Mader \(^{17}\).

Catalytic hydrogen currents of low molecular weight thiols such as cysteine, cysteine ethyl ester, cysteamine, thioglycollic acid, thiosalicylic acid in buffers such as borax, boric acid, tris-hydrochloric acid, phenol-sodium phenolate, ammonium chloride - ammonium hydroxide etc. in the presence of Co(II) ions exhibit typical kinetic characteristics and the rate determining step is a chemical process \(^{18}\).

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 \(^{19}\). The nature of the polarographic protein waves in ammonia buffer containing hexamine cobalt chloride was studied in detail by Kuznetsov \(^{20}\) and Senda et al \(^{21-23}\). 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 catalytic activity of the protein - zero valence cobalt complex increases with the increase in temperature.
From the above observations it is seen that the catalytic evolution of hydrogen on DME from solution of thiols or disulphides / or proteins containing metal ions was an electrochemical reaction, which attracted attention of many experimentalists resulting in an extensive and voluminous literature\textsuperscript{24-31}.

Inspite of such a great effort which has been devoted to the study to the nature of catalytic hydrogen currents, the detailed mechanism for these catalytic currents is not fully understood so far. A few workers have suggested a brief mechanism and the important factors involved in these reactions. The mechanisms of Mader and his associates\textsuperscript{18} for Co(II)-thiol complexes are found to be satisfactory as they incorporate almost all mechanisms reported earlier and also follow the general reactions suggested for catalytic hydrogen waves. According to them catalytic hydrogen currents are of two types, namely, Brdicka current having one maximum and non-Brdicka catalytic hydrogen currents with two maxima. It is seen that low molecular weight thiols under certain experimental conditions give Brdicka currents whereas mercapto-aniline and related aromatic compounds give non-Brdicka currents and are identified with notations A and B at a positive potentials of limiting current plateau of metal ion. Both Brdicka and non-Brdicka catalytic hydrogen waves can be observed with all thiols under suitable experimental conditions. In both the cases the rate determining chemical reaction is the protonation of the catalytically active species. Based on various effects such as pH, temperature, ionic strength etc., mechanisms are suggested for these two types of currents.
In the case of Brdicka currents, at less than 20% of saturation value (maximum current) 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.

\[
\begin{align*}
\text{[Co}^{\text{II}} \text{(RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_{\text{bulk}} & \xrightarrow{\text{diffusion}} \text{[Co}^{\text{II}} \text{(RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0 \quad (1) \\
\text{[Co}^{\text{II}} \text{(RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0 & \xrightarrow{2e^-} \text{[Co}^{\text{0}} \text{(RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0 \quad (2) \\
\text{[Co}^{\text{0}} \text{(RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0 + BH^+ & \xrightarrow{\text{Protonation}} \text{[Co}^{\text{0}} \text{(RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0 + \text{B} \quad (3) \\
\text{[Co}^{\text{0}} \text{(RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0 & \xrightarrow{e^-} \text{[Co}^{\text{0}} \text{(RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0 + \frac{1}{2} \text{H}_2 \quad (4)
\end{align*}
\]

\[\text{[Co(II) (RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0\] 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 and 4 mentioned above.

\[
\begin{align*}
\text{[Co(II) (D)}_m \text{(H}_2\text{O)}_n \text{]}_{\text{bulk}} & \xrightarrow{\text{Complexation}} \text{[Co(II) (D)}_m \text{(H}_2\text{O)}_n \text{]}_0 \\

\text{[Co(II) (RS)}_x \text{(D)}_y \text{(H}_2\text{O)}_z \text{]}_0
\end{align*}
\]
where D refers to basic buffer constituent and subscript zero, refers to the surface of the electrode.

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 has an adsorption kinetic character.

\[
\begin{align*}
[\text{Co}^{\text{II}}_{x} (\text{RS})_{y} (\text{H}_{2}\text{O})_{z}]_{\text{bulk}} & \xrightarrow{\text{diffusion}} [\text{Co}^{\text{II}}_{x} (\text{RS})_{y} (\text{H}_{2}\text{O})_{z}]_{0} \quad (5) \\
[\text{Co}^{\text{II}}_{x} (\text{RS})_{y} (\text{H}_{2}\text{O})_{z}]_{0} + \text{BH}^{+} & \xrightarrow{\text{Protonation}} [\text{Co}^{\text{II}}_{x} (\text{RS})_{y} (\text{H}_{2}\text{O})_{z} \text{H}^{+}]_{0} + \text{B} \quad (6) \\
[\text{Co}^{\text{II}}_{x} (\text{RS})_{y} (\text{H}_{2}\text{O})_{z} \text{H}^{+}]_{0} + e^{-} & \xrightarrow{\text{diffusion}} [\text{Co}^{\text{II}}_{x} (\text{RS})_{y} (\text{H}_{2}\text{O})_{z}]_{0} + \frac{1}{2} \text{H}_{2} \quad (7)
\end{align*}
\]

The origin of maximum 'B' in the second type of non-Brdicka current is stated to be from the decomposition of the cobalt(0) - thioate complex into thiol and cobalt(0) metal. The freshly deposited metallic cobalt liberates molecular hydrogen and thiolate ion, RS becomes RSH. The wave is surface kinetic in character.

\[
\begin{align*}
[\text{Co}^{0}_{x} (\text{RS})_{y} (\text{H}_{2}\text{O})_{z}]_{0} & \xrightarrow{\text{decomposition}} x \text{RS}^{-} + \text{Co}(0) \text{ metal} + \ldots \\
+ \text{H}^{+} & \xrightarrow{e^{-}} \frac{1}{2} \text{H}_{2} + \text{H}^{+} \\
\text{RS} \text{H}_{2}O & \xrightarrow{e^{-}} \text{RSH}
\end{align*}
\]
The direct discharge of hydronium ion on the stabilized atom of metallic cobalt on the surface at the mercury may also be from the thiol-free species existing in solution before complexation.

According to these schemes current should be linearly proportional to Co(II) concentration and/or thiol concentration which is not true as they (particularly currents A and C) obey an expression similar in form to the Langmuir adsorption isotherm. Another drawback in the scheme, particularly with current B, is that a direct reaction of Co(0) with RS to form Co(0) - RS is very slow and does not occur under experimental conditions used, when life period of Co(0) is short. Further, the scheme does not talk of other functional groups responsible for the catalytic currents.

After the general scheme is proposed by Mader et al\textsuperscript{18} in 1982 there are hardly any references to explain the setbacks seen in it. The few who attempted have only confirmed that the electrode reactions are preceded by adsorption of the catalyst on the mercury (DME) and have not proposed either scheme or mechanism.
Cyclic Voltammetry

Cyclic voltammetry is an important technique which provides the means to examine the nature or pathway of an electrochemical reaction in detail.

As the name implies, it is a cyclic or an isosceles triangular voltage wave form, applied to a micro electrode, having a voltage scan-rate ranging from 5 mv/sec to 1000 v/sec. The current potential curves at stationary electrodes (Platinum electrode, hanging mercury drop electrode – HMDE, carbon paste electrode – CPE etc) in unstirred solutions depend upon the rate of change of applied potential. At a constant potential, the reduction or oxidation of an electroactive substance depletes a layer of solution that extends further from the electrode surface into the bulk of the solution as time proceeds, resulting in a current decrease.

The potential of the working electrode is varied linearly with time allowing one to scan in the cathodic (or anodic) direction and observe peaks due to reduction (or oxidation) of a substrate, followed by scan reversal. Generally, linear diffusional conditions should be employed in cyclic voltammetry. Fast scan rates minimize diffusional problems and a detailed discussion of the diffusion problems is given in the monograph by Adams. This technique was established by Matheson and Nichols and later by Sevcik. Ceramak showed the well defined current potential curves for slow polarizations at stationary mercury electrodes. A series of papers by
Shain and Co-workers\textsuperscript{36-38} present a detailed development of the theory of cyclic voltammetry.

The utility of the technique was worked out by Randles\textsuperscript{39} for reversible process and Delahay\textsuperscript{40} for irreversible processes. Cyclic voltammetry was also used in the identification of intermediate products in electrode processes\textsuperscript{41,42}.

The peak current in a reversible process is quantitatively expressed by

\[ i_p = K n^{1/2} AD^{1/2} C v^{1/2} \]

Where

- \( i_p \) = peak current, amperes cm\(^2\)
- \( n \) = number of electrons involved in the electrode process
- \( A \) = area of the electrode, cm\(^2\)
- \( D \) = diffusion coefficient of the electroactive species in cm\(^2\) sec\(^{-1}\)
- \( C \) = concentration, mole cm\(^3\)
- \( v \) = scan rate of the applied linear voltage sweep in v/sec and
- \( K \) = Randles–Sevcik constant

Delahay\textsuperscript{40} indicated 2.72 x 10\(^5\) as the most reliable value for \( K \) in the case of reversible processes.

For irreversible processes,

\[ i_p = 3.01 \times 10^5 \, n \, (\alpha \, na)^{1/2} \, AD^{1/2} \, C v^{1/2} \]
where
\[ \alpha = \text{transfer co-efficient} \]
\[ n_a = \text{number of electrons involved in the rate determining step} \]

The equation,
\[ E_p (\text{anodic}) - E_p (\text{cathodic}) = 0.058/n \text{ volts} \]
\[ E_p - E_p / 2 = 0.059/\nu \text{ volts} \]

is given by Mastuda and Ayabe\(^4\) for reversible systems.

A totally irreversible system may not show a peak in the reverse scan. For such systems the relation is
\[ E_{p/2} - E_p = 0.048 / \alpha n_a \text{ volts} \]

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

Expression for quasireversible cases are more complicated as it involves both diffusion and charge transfer kinetics and is given by Bauer\(^4\). The peak current divided by the square root of scan rate is usually termed as current function, is given by the expression
\[ i_p / \nu^{1/2} \quad C = k' \]

Where \( k' \) is composed of all the constants of the equation 1. The current function when plotted against \( \nu^{1/2} \) gives very convenient means of detecting chemical reactions.
The chemical reactions are of two types, chemical reaction following charge transfer and preceding charge transfer. The important parameters required to characterize the nature of these reactions are presented here briefly.

a. **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 \( i_p^a / i_p^c \) decreases from unity as \( v \) increases.

b. **Irreversible Chemical Reaction Following Charge Transfer**
   
i. \( E_p \) shifts cathodically, by \( 30 / n \) mV at low \( v \), a lesser shift noted at higher values of \( v \).
   
ii. The current function, \( i_p / v^{1/2} \) is independent of \( v \).
   
iii. The anodic to cathodic current ratio increases towards unity as \( v \) is increased.

c. **Reversible Chemical Reaction Preceding Charge Transfer**
   
i. \( E_p \) shifts anodically with an increase in \( v \).
   
ii. The current function, \( i_p / v^{1/3} \) decreases as \( v \) increases.
   
iii. The anodic to cathodic current ratio is generally greater than unity and increases as \( v \) increases with a value of unity approached at lower values of \( v \).
d. **Irreversible Chemical Reaction Preceding Charge Transfer**

i. $E_p$ shifts cathodically by $30 / n \text{ mV}$ for a 10-fold increase in $v$.

ii. The current function $i_r / v^{1/2}$ decreases with an increase in scan rate, $v$.

iii. There is no current on the reverse scan.

**Catalytic Regeneration of Reactant**

Nicholson and Shain\textsuperscript{36,37} proposed the catalytic mechanism for the cyclic experiment, assuming that the charge transfer is reversible. Saveant and Vianello\textsuperscript{45} also considered the case of reversible charge transfer. Nicholson and Shain have examined $(i_l) / (i_r)$ as a function of the kinetic parameter. The catalytic reaction following an irreversible charge transfer reaction has also been treated by Nicholson and Shain.

The diagnostic criteria for a catalytic reaction is

i. $E_p$ shifts anodically with an increase in $v$ by an extent which goes through a maximum of $60/n \text{ mV}$ per 10-fold increase in $v$.

ii. The current function, $i_r / v^{1/2}$ increases at lower values of $v$ and becomes independent of $v$.

iii. The anodic to cathodic current ratio is unity

**Adsorption-the cyclic voltammetric behaviour**

The theory of cyclic voltammetry has been extended to study the adsorption phenomenon of electrochemical systems. The cyclic voltammetric behaviour for the adsorption processes was given by Wopschall and Shain\textsuperscript{46} in detail.
The nature of the adsorption isotherm known as Langmuir isotherm is given by

\[ T = \frac{T^* C}{K + C} \]  

(7)

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

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

(8)

Where the value of \( K \) is dependent on a number of experimental conditions like solvent, electrode surface, temperature etc., and is a function of electrode potential when the rest of the conditions held constant\textsuperscript{47}.

The nature of the effects of adsorption processes on the cyclic voltammetric response has been treated by Wopschall and Shain.\textsuperscript{48-49} The possible cases are weak or strong adsorption of either reactant or product.

**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 potentials of the two responses $\Delta E_p$ increases.

The qualitative characterisation of strong adsorption of the product is known by variation of the response with bulk concentration and scan rate. At very low concentrations the reduction to the adsorbed state is the primary process. As the concentration is increased the relative height of the adsorption response to the diffusion-controlled response decreases. 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 the responses obtained is cathodic to the diffusion-controlled response. 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 diffusion process predominates at low scan rates whereas the adsorption process predominates at high scan rates.
Weak Adsorption of the Reactant

When the electroactive species is only weakly adsorbed, the nature of the response is different from that of the strong adsorption. 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 hence, a more pronounced peak shape for both the cathodic and anodic scans is exhibited. The response with increasing scan rate should increase in the presence of adsorption relative to that of the purely diffusion-controlled case. 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 product is not as important as weak adsorption of reactant because this has little effect on the cathodic scan. With increasing scan rate the cathodic peak shifts anodically and exhibits a decrease in peak height. On the other hand, the anodic peak increases markedly with scan rate and becomes more symmetrical.

Many electrochemical reactions of organic compounds involve both coupled chemical reactions and adsorption. These two processes reflect their presence on each other and only a semi empirical method was developed by Wopschall and Shain. 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. However, the nature of the effects of adsorption must be carefully examined with respect to the effects of any chemical reaction and their interactions included in arriving at diagnostic conclusions.

**Catalytic currents in Trace Analysis**

Many analytical techniques are available for carrying out trace analysis namely, atomic absorption spectroscopy, neutron activation analysis, fluorometry, flame spectrometry, anodic stripping voltammetry etc. All these require special experimental conditions.

Among all the analytical techniques, d.c. polarography is the most preferred technique for trace element analysis because of following features. They are, (i) high sensitivity, (ii) selectivity, (iii) low cost of equipment, (iv) easy handling of equipment and (v) applicability for wide range of trace elements.

The catalytic hydrogen waves of thiamine were used for its determination in ammonical media in the presence of cobalt(II) or cobalt(III) by Lopez Fonsica. A new catalytic current other than Brdicka current was reported by Anzerbacher and Kalous for cysteine in cobalt(II) solution in an ammoniacal buffer on an HMDE. This result was attributed to the pre-
electrolysis of Co(II) which is deposited on the electrode. This deposited cobalt was found to be different in nature in the presence of cysteine due to existence of various Co(II) complexes in the solution which were reduced at different potentials.

The effect of thiourea and its alkyl derivatives on the reduction of various cations as Ni(II), Co(II) and Cu(II) was studied in neutral medium by classical and pulse polarography by Vanlaethiem-Meuree, who indicated that these sulfur compounds give catalytic hydrogen currents similar to those by proteins. A similar catalytic hydrogen wave of cysteine and thioglycolic acid in ammoniacal solution containing cobalt(II) salt were reported by Babkin et al. Kadleccek et al. showed that the catalytic activity of structurally similar thiols decreased with decreasing values of the stability constants of the complexes with Co(II) ions. The catalytic hydrogen waves caused by mercapto derivatives formed in a reduction process of organic sulfoxides and sulfides at DME in aqueous ethanol was indicated by Johansson and Wendsjo. They explained the behaviour of catalytic waves as a function of the adsorptivity of the catalysts and their polarization in the high electric field of the double-layer. The paper also mentioned that in the case of sulfoxides all the products acted as catalysts and gave two catalytic waves corresponding to pyridine and mercapto derivatives, whereas sulfide derivatives gave only one catalytic wave corresponding to the product, 2-methyl pyridine.
Kolthoff and his co-workers studied the catalytic hydrogen currents observed with native and treated bovine serum albumin (BSA) in various buffers such as ammonia, borate and tris buffer. The paper clearly indicates that both nitrogenous and sulfhydryl groups of BSA and treated BSA were responsible for the appearance of catalytic hydrogen waves which were also referred to as pre-sodium waves. Catalytic hydrogen currents due to the presence of heme and -SH groups in horse myoglobins, sperm whale, bovine and human haemoglobins in buffer solutions containing cobalt salts at DME and HMDE were reported by Kinoshita et al. A direct correlation between the number of -SH group content of bovine or human haemoglobin and the catalytic hydrogen currents was established by Kuik et al. A similar correlation between the number of -SH groups and the catalytic current was shown by Kuik and Krassowski using solution containing bovine, ovine, dog, human, rabbit, pigeon haemoglobins and bovine or human mathaemoglobins in several ammonia and cobalt chloride concentrations where linear correlation between the current and number of -SH groups in the molecules were shown.

The catalytic hydrogen wave of ethyl thioglycollate in ammonical cobaltous chloride solution was presumed to be due to complex of cobalt thioglycollate by Saxena and Chaturvedi. The polarogram of cobalt in ammonia buffer in the presence of thiols at HMDE after preelectrolysis, as recorded by Kadlecek et al. clearly indicated a catalytic hydrogen wave which was attributed to a deposit of cobalt(O) on mercury, which lowered the
overvoltage of hydrogen and gave the catalytic hydrogen wave. The catalytic activity of three cysteine-containing dipeptides in ammonical medium in the presence of cobalt chloride was investigated by Kadlecek and Kalous\textsuperscript{62}. The behaviour of cobalt(II) at DME in a borax buffer in presence of a number of pyrimidine thiols was examined by Lopez et al\textsuperscript{63}. The results obtained indicated that the 1:1 complex was responsible for the catalytic prewave through adsorption on mercury of the reduction product of the complex.

Galvez et al\textsuperscript{64} suggested a mechanism for production of catalytic hydrogen wave obtained with dimethyl dithiocarbamate in the presence of cobalt(II) in ammonia buffer. According to them, the reduction product of Co(II) complex of thio compound, Co(0) adsorbed over mercury was responsible for the catalytic hydrogen wave.

Periz Ruiz and Martinez Moreno\textsuperscript{65} observed two catalytic hydrogen currents in the reduction of 2,2-dithiobenzoic acid in the presence of cobalt(II) at DME. The first wave was assumed to result from protonation of adsorbed cobalt(0)-ligand complex while the second wave was attributed to the lowering of hydrogen overvoltage by the adsorbed metallic cobalt on the mercury. The first wave was utilized for the determination of the thio compound and in the amperometric titration of cobalt(II) with EDTA. Zhao and Wang\textsuperscript{66} designed a method for the determination of cobalt in various samples upto $1 \times 10^{-10}$ M by catalytic polarography in phenanthroline-thiourea ethanol amine system.
A novel method based on the accumulation of cobalt complex, [Co SCN NO]⁺ on HMDE was described by Gao et al. down to 0.3 mM concentration of the metal using differential pulse voltammetry.

Polarographic catalytic hydrogen waves of thio compounds are observed not only with Co(II) or Co(III) but also with a few other transition metal ions. Bis hydroxymethyl dithiocarbamate and dimethyl dithiocarbamate in acetate buffer in the presence of Mn(II) and Fe(II) in aqueous ethanol and aqueous DMF media were found to give catalytic hydrogen waves by Budnikov et al. These waves were used in the determination of traces of the Fungicide Ferbam in the range of 0.5 to 5x10⁻³ µg/ml. Co(III) and Fe(III) with thiosemicarbazones of pyruvic acid and benzoyl formic acid gave catalytic hydrogen waves, as described by Toropova et al.

Budnikov et al. obtained catalytic hydrogen currents at DME in solutions of nickel and cobalt complexes with (carboxy-methyl) and (carboxyl-ethyl) dithiocarbamates in KCl medium. The current was rectilinearly related to Co concentration in the range of 5 to 40 µM. The catalytic hydrogen waves of Co and Ni complexes with alkyl xanthates of the general formula M (ROOC₂₅) (where R = Me, Et, Pr, Iso-pr, Bu and n-pentyl) and dialkyl dithiophosphates of the type M [(RO)₂PS₂] x (where R is Et and Iso-Bu) were studied at DME in DMF and EtOH-H₂O solutions using Et₄NClO₄ as supporting electrolyte.
The complexes of Fe(II), Co(II) and Ni(II) with bis-(2-hydroxyethyl) dithiocarbamate in H2O-EtOH medium in acetate buffer produced catalytic hydrogen waves whose currents were proportional to the concentration of metal ions in the range of 5mM to 0.5mM. The catalytic hydrogen currents of Fe(III), Co(II) and Ni(II) with ethyl xanthate in acetate buffer was reported by Frolova et al. by extraction voltammetry. The method was applied to waste-water analysis.

The catalytic wave of Ni(II)-cystein system in ammonia buffer revealed three peaks in the potential range where catalytic reduction of hydrogen occurred. According to Kuik, the shape and height of these peaks depended on the molar ratio of Ni and cysteine, the composition of the buffer, temperature etc. The catalytic hydrogen waves produced by nickel in cysteine containing acetate buffer was examined by Banica and Calusaru. The method was compared spectrophotometrically and found that Ni(II)-complexes with cysteine were involved in electrode reactions which acted as catalysts for hydrogen evolution. The same was identified using isotropically different solutions and was explained in the form of two possible reactions, the first was considered as protonation of the amino group of cysteine and the second as the reaction with Ni(II) to give a reducible complex which acted as a catalyst. Nickel(II) was also found to give two catalytic hydrogen waves in the form of humps by nickel-merapto benzoazole system. A reaction scheme for catalytic hydrogen prewave due to nickel-glutathione at pH 7.0 was suggested by Elena et al.
Simultaneous determination of copper, nickel, cobalt and cadmium in human hair and tea sample without interference with each other using catalytic hydrogen waves due to 1-(2-quinolylazo)-2,7-dihydroxy naphthalene complexes was reported by Zhang Zhengqi et al.\(^2\).

The polarographic wave of Cu(II) in the presence of H\(_2\)SO\(_4\) and thiourea was reported by Biernat and Syzmaszek\(^4\) who showed that the wave was due to the catalytic reduction of hydrogen ions at low overvoltage. An indirect polarographic method for the determination of Cu(II) based on the highly stable complex, Cu(II)-salicylaldehyde thiosemicarbazone was developed by Revathi and Palaniappan\(^5\). The method was applied for the micro determination of copper in high purity reagents upto 0.5 ppm. The polarogram of Cu(II) in HCl-thioglycollic acid-1,10-phenanthroline exhibited an adsorptive catalytic wave which was applied for trace amounts of Cu in waste and natural waters, the limit of detection was 0.03 \(\mu\)g/ml\(^6\).

The heterocyclic azo complexes of copper on accumulation on static mercury drop electrode provided the basis for the direct cathodic stripping voltammetric analysis\(^7\). The polarographic determination of indium with thioglycollic acid and 2,2'-bipyridyl in acetate buffer was proposed by Du et al\(^8\). The limit of determination was 5ng ml\(^{-1}\) and was used for the determination of trace quantity of indium in waste waters. Simultaneous determination of traces of cadmium and indium was performed by Du and Huang\(^9\) using acetate buffer in the presence of thioglycollic acid-2,2'-bipyridyl-diphenylguanidine. The detection limits were \(3 \times 10^{-9}\) mol l\(^{-1}\) and
1.2 \times 10^{-9} \text{ mol l}^{-1} \text{ for Cd and In respectively and the method was applied to industrial waste water analysis.}

Medyantseva et al.\textsuperscript{67} observed catalytic hydrogen waves of ruthenium and rhodium in acidic media in presence of diethyl dithiocarbamate in dimethylformamide. The method was applied to the analysis of Cu-Ni sulfide ore and the limit of detection was 20nM for Rh and 8nM for Ru. The rhodium-thiosemicarbazide complexes were studied by IR and UV spectroscopy and polarography. The 1:2 and 1:3 complexes catalyzed the reduction of hydrogen ions at DME and gave catalytic hydrogen waves which was used for quantitative determination of rhodium\textsuperscript{68}. The factors that affected the catalytic hydrogen currents arising during the reaction of rhodium with thiosemicarbazide were studied and optimum conditions for the determination of Rh was developed by Ezerskaya et al.\textsuperscript{69}. The catalytic hydrogen currents due to complexes of rhodium with organic thio compounds were studied to improve the sensitivity of the method for the determination of rhodium\textsuperscript{90}. The polarogram of rhodium -DL-2,3,5,6-tetrahydro-6-phenyl imidazothiazole chloride showed the formation of 1:1 complex which was adsorbed on the mercury electrode and catalyzed the proton discharge responsible for the catalytic hydrogen wave\textsuperscript{91}.

A stable complex of rhodium with dichloro-pyridyl azo-dimethyl amino aniline in acetate buffer at pH 5.0 was used by Zhang Zhanyi et al.\textsuperscript{92} for the determination of rhodium in parts per trillion level. The polarogram of palladium at pH 1.5 in the presence of thiosemicarbazide indicated the
presence of catalytic hydrogen wave whose current was proportional to palladium concentration in the range, 0.5 to 11.0 ppm of the metal.

A new catalytic polarographic method was reported by Dezhong Dan and June Re for trace amounts of tungsten in the concentration range 0.004-1.4 μg/ml in acidic medium using mercaptobenzothiazole complex.

Shi et al. developed a catalytic polarographic method for the determination of trace germanium in vegetables using the polarographic complex of germanium (IV) - pyrogalol - sodium bromate.

Weng Shuahao et al. developed a method which is based on the catalytic effect of Fe³⁺ on the oxidation reaction between acid chrome blue and potassium bromate in sulphuric acid medium at 100°C and in 0.08 mol/L NH₄ OH - 0.01 mol/L (NH₄)₂ SO₄ 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 2×10⁻⁹ g/ml.

Molybdenum in human hair was determined by catalytic polarography in a base solution containing sulphuric acid 0.032 M, Na₂SO₄ 0.11M, hydroxy phenyl acetic acid 0.048 M and NaClO₃ 0.63 M. Weixian You and his workers developed a method polarographic adsorptive catalytic wave of Ge(IV) - pyrocatechol violet - V(IV) systems. Xiangchuchuan Zhou et al.,
described a new polarographic adsorption catalytic wave for the determination of trace Te in smog dust and wheat flour.

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 μg/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.

Wang Shuhao developed a method for trace amounts copper with catalytic polarographic detection.

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.

Karvoda studied the adsorption in polarographic / voltammetric environmental analysis. Polarographic adsorption catalytic wave of Tin(IV)-pyrogallolred-V(IV) - sodium dodecyl sulfonate system was developed by Long Hui et al. Wang Lizeng and his co-workers studied the polarographic investigation of the catalytical adsorptive complex behaviour of trace iron. Xuxian et al. determined the adsorptive wave of lead-phencadion by polarography. Polarographic adsorptive catalytic wave of Tin(IV)-3,4-dihydroxybenzoic acid - V(IV) system was studied by Long Hui. Yuyu Volvodin et al. developed the electrocatalytic reduction of Trifluororiodomethane in the presence of cobaloximes. New aspects of brdicka reaction of low molecular thiols at low rate of potential scan using voltammetry by M. Heyrovsky.
In the laboratories the idea of calusaru and Kuta\textsuperscript{114} was already practiced by using simplest molecules with only -SH functional groups using DME (D.C. Polarography) and HMDE (cyclic voltammetry). These experiments resulted in few publications suggesting the third mechanism due to decomposition of metal-ligand complex to give zero valent metal complex that remains adsorbed at the electrode and gets protonated to get reduced subsequently to give molecular hydrogen. These ideas are supported by Heyrovsky et al.\textsuperscript{115}

Incidentally, our experience on catalytic hydrogen currents has led us to develop simple and sensitive analytical methods for monitoring trace metal ions in various matrices such as natural water, industrial effluents, agricultural products, food items, soils etc. The results of CHCs using simple technique like D.C. polarography were compared with AAS\textsuperscript{116,142}.

Polarographic catalytic currents that have been used for the quantitative analysis of metal ions at trace levels have been reviewed here except those 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. Many thio compounds have been utilized in these laboratories for the analysis of metal ions [Cu(II), Co(II), Cr(VI), Ni(II), Fe(II) and Mn(II)] and the assessment of these ions in various environments samples, ores, alloys, biological, agricultural and pharmaceutical samples.
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