UNIT 7  VOLTAMMETRY

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7.1  INTRODUCTION

This is the first unit of the electroanalytical methods course. We will start our
discussion by defining what is voltammetry and then continue our discussion with the
different methods of voltammetry. We will discuss the sampled DC polarography and
hydrodynamic voltammetry. We will also discuss in detail the pulse methods viz.
Normal pulse polarography, Differential pulse polarography and Square wave
polarography/voltammetry.

Then cyclic voltammetry (CV) will be discussed along with a diagnostic test to decide
reversibility of a redox reaction. Finally the instrumentation involving CV will be
explained.

Objectives
After studying this unit, you should be able to:
•  define voltammetry,
•  discuss the electrodes and processes of voltammetry,
•  discuss the dc methods in voltammetry,
•  explain the pulse methods of voltammetry,
•  explain anodic, cathodic and adsorptive stripping methods in voltammetry,
•  discuss the alternating current methods in voltammetry,
•  name the instruments involved in voltammetry, and
•  select a suitable method of voltammetry for the analysis of a particular sample.
7.2 ELECTRODES AND PROCESSES

Voltammetry is the general name given to a group of electroanalytical methods in which the current is measured as a function of applied potential wherein the polarization of the indicator or working electrode is enhanced. For this, the working electrodes used in voltammetry are generally microelectrodes having surface area of few square micrometers to square millimeters. This field has been developed from Polarography (developed by Heyrovsky); which is a particular type of voltammetry, which used a dropping mercury electrode as the working micro-electrode. Voltammetry includes all techniques in which the current potential measurements are made at stationary and fixed electrodes. After studying this unit, you will be in a position to understand different voltammetric techniques.

The measurement of a current is done when the complete concentration polarization takes place in an electrochemical cell. Voltammetry has developed from polarography. Polarography, as will be discussed in Unit 8, uses the DME as the working electrode. In voltammetry, the process of polarization is enhanced by using ‘microelectrodes’ as the working electrodes.

Thus, we can say that the electrochemical method in which the current is measured as a function of the potential applied to a microelectrode is known as voltammetry. These electrodes may be solid like gold, platinum and glassy carbon or mercury. If the electrode is formed by a drop of mercury dropping from a fine glass capillary, the technique is called “Polarography” (discussed in detail in Unit 8).

Other forms of working electrodes used are hanging mercury dropping electrode (HMDE), static mercury drop electrode (SMDE), thin mercury film electrode (TMFE), glassy carbon electrode (GCE), carbon paste electrode (CPE), etc. Working electrodes made of noble metals are used less frequently. Some electrodes are given in Fig. 7.1.

Processes

Various methods are assigned to the terms voltammetry and polarography which differ in the measuring techniques and the type of electric potential used to excite the determination process.

Voltammetry is widely used for the quantitative analysis of trace metal ions at micro level. This study of redox processes lead to the qualitative and quantitative analysis of heavy metals and some organic substances in solution. In addition to this aspect this technique is quite versatile for research purpose in the fields of

i) redox processes
ii) electron transfer mechanisms at chemically modified electrode surfaces
iii) adsorption processes
iv) corrosion proof materials
v) new electronic processes for chemical industries
vi) production of new types of batteries that can store large quantities of energy

More recently this technique is gaining more importance in the technique of production of pharmaceutical materials with the introduction of principles of green chemistry.
Figure 7.1 Some common types of microelectrodes: (a) a disk electrode; (b) a mercury hanging drop electrode; (c) a dropping mercury electrode; (d) a static mercury dropping electrode.
7.3 COMMON VOLTAMMETRIC METHODS

The most widely used voltammetric methods are

A) Direct current methods
   i) D.C. Polarography (discussed in detail in Unit 8).
   ii) Linear sweep voltammetry
   iii) Sampled D.C. Polarography
   iv) Hydrodynamic voltammetry

B) Pulse methods
   v) Normal Pulse voltammetry
   vi) Differential Pulse voltammetry
   vii) Square wave voltammetry
   viii) Cyclic voltammetry

C) Stripping voltammetry
   ix) Anodic stripping voltammetry
   x) Cathodic stripping voltammetry
   xi) Adsorptive stripping voltammetry

D) Alternating current methods

7.4 DIRECT METHODS

Under this category linear sweep voltammetry and hydrodynamic voltammetry will be discussed in addition to the sampled D.C. polarography.

7.4.1 Linear Sweep Voltammetry

The simplest type of voltammetry is called Linear Sweep Voltammetry (LSV). In this technique, the potential of the working electrode is varied linearly as a function of time and the current response is recorded. The scan rates are relatively slow, i.e. less than 5 mV/sec, which allows the movement of fresh analyte to reach the electrode surface, so that the electrode is always in equilibrium with the bulk solution. Consider a one electron reduction reaction.

\[ \text{A} + e^- = \text{B} \]

which obeys Nernst equation.

Here, E is the potential of the working electrode; \( E^\circ \) is the standard reduction potential of A.

If a solution containing only A is taken in a cell and an applied potential of about 200 mV is applied, then a miniscule amount of current will flow to convert a small amount of A to B so that Nernst equation is obeyed at the electrode surface. The amount of current increases as the potential approached the \( E^\circ \), when E becomes equal to \( E^\circ \), \([B] = [A]\) at the electrode surface or in other words, at \( E^\circ \), half of the total A reaching the electrode is converted to B, so that the current is half way to its limiting current.
As E is lowered further, all the A is converted to B, as soon as it reaches the electrode.

![Fig. 7.2: Normal DC polarography](image)

An important feature of this technique is that largest change in slope occurs around \( E^\circ \). The value of the potential corresponding to the point where the current is exactly half of the total current is known as half wave potential (\( E_{1/2} \)) and this value is used to identify the unknown species (qualitative analysis) and the difference in the value of the current from the start to the maximum value is known as limiting current, i.e. sum of migration current + residual current and diffusion current, but after elimination of the first two the diffusion current (\( i_d \)) that is directly proportional to the concentration of the analyte and is used for its analytical determination (quantitative analysis)

\[
i_d = Kc_A
\]

where \( c_A \) is the analyte concentration and K is a constant

![Fig. 7.3: Linear Sweep Voltammogram](image)

Polarographic determinations with higher sensitivity can be achieved if the ratio of \( i_d/i_c \) is improved by other measuring techniques by increasing the Faradaic current or reducing the condenser current. These modifications gave rise to sampled DC polarography and pulse methods.

In normal DC polarography, the electrode area is not constant and hence the current fluctuates with the life time of each drop within some range as shown in Fig.7.3. This problem can be alleviated by measuring the current once at the end of the life time of each drop and this method is called Sampled DC Polarography or Tast Polarography.

### 7.4.2 Sampled DC Polarography

In this technique instead of recording the current continuously, it was sampled for a 5 millisecond period just before the drop falls. Between the sampling periods, the recorder was maintained at its last current level by means of a sample and hold circuit.
The major advantage of this current sampling is that it substantially reduces large current fluctuations due to continuous growth and fall of the drops at dropping electrode. From Fig. 7.3, it can be seen that the current near the end of the life of a drop is nearly constant and it is this current only that is measured in the current sampled technique resulting in a smooth curve with very little current fluctuations.

**Fig. 7.4: Sampled DC Polarogram**

LSV in which the solution or the electrode is kept in motion is called hydrodynamic voltammetry.

**SAQ 1**

a) Why does the current fluctuate with the life time of each drop as shown in Fig.7.3?

b) What do you mean by Tast Polarography?

**SAQ 2**

What are the major advantages of current sampling in Sampled DC polarography?

### 7.4.3 Hydrodynamic Voltammetry

In hydrodynamic voltammetry current is measured as a function of the potential applied to a solid working electrode kept in stirring solution. Linear scan profiles are used while the solution is in motion towards the electrode.

The cell has three electrodes, the working electrode (usually mercury coated electrodes); a reference electrode (SCE) and a counter electrode (Pt coil). The current in the cell passes between the working electrode and counter electrode.

The electroactive substance undergoing electrode reactions at micro electrode is brought to the electrode by three modes:

i) migration of charged ions under the influence of an electric field due to attraction of the electrode that has a positive or negative charge.
ii) convection resulting from stirring or vibration.

iii) diffusion due to concentration gradient established near electrode during the reaction.

This is the current that is proportional to the concentration of electroactive substance and is given by

\[ i_l = nFAD \frac{c_a}{\delta} \quad \text{... (7.2)} \]

where

- \( c_a \) = Concentration of analyte,
- \( n \) = number of electrons,
- \( F \) = Faraday constant,
- \( A \) = Area of the electrode surface,
- \( D \) = Diffusion coefficient of the analyte,
- \( i_l \) = Limiting current,
- \( \delta \) = thickness of Nernst layer

![A three electrode cell for hydrodynamic voltammetry](image)

**Fig. 7.5: A three electrode cell for hydrodynamic voltammetry**

Here, stirring is accomplished using a magnetic stirrer but in some other cases the electrode is rotated at a constant high speed in the solution thus providing a stirring action. The obtained voltammogram is a wave and the current voltage plot is characterized by an initial residual current that grows up with increasing potential till the \( E_{1/2} \) and then slowly increases till a stationary level is reached. At this value of potential the ions reaching the electrode discharge immediately thus the concentration of the analyte in the diffusion layer is almost nil. The continuous flowing of ions into the diffusion layer due to stirring maintain a constant current.

Another way of carrying out this technique involves the flowing of analyte solution through a tube in which the microelectrode is fixed. This technique has been used as a voltammetric detector in HPLC.

Some important applications of this technique include the detection and determination of oxygen and chemical species like glucose, lactose and sucrose. This detector has also been used in fundamental studies in electrochemistry and detection of end points in electrometric and volumetric titrations.
SAQ 3

a) What do you mean by Hydrodynamic voltammetry?

b) In Hydrodynamic voltammetry, how the flow of analyte solution is carried out?

7.5 PULSE METHODS

The sensitivity of linear scan voltammetry or polarography is limited by charging current which is large initially in the drop life. The slowness, inconvenient apparatus and poor detection limits of linear scan voltammetry or polarography were the reasons for its decline. The sensitivity of these two methods is improved by pulse methods by about 6.5 times by eliminating charging current. The current in these methods is measured at a time when the difference between the Faradaic current and the interfering charging current is large. There are four important pulse methods namely

i) Normal pulse voltammetry/polarography

ii) Differential pulse voltammetry/polarography

iii) Square wave voltammetry

iv) Cyclic voltammetry

The potential excitation signals used in different voltammetric methods are given in Fig.7.6 and the individual methods are discussed in the following sections.

7.5.1 Normal Pulse Polarography (NPP)

In this technique, the potential is altered by using square wave potential pulses and is applied only briefly for about 50 ms before each current measurement. The data obtained have the same shape as LSV and the sensitivity is increased. The dropping mercury electrode is held at the initial potential until there are only about 60 ms left in the life time of the drop. Thus very little electrolysis and depletion occurs. During the last 15 ms, before the expiration of the pulse time, the current is measured. Each new drop is stepped up to a greater potential and is measured after about a 40 ms delay, a sensitivity improvement of approximately three times is observed.

7.5.2 Differential Pulse Polarography (DPP)

A still greater improvement is reached by using the programming wave form as shown in Fig. 7.6. In this technique a 50 mv pulse is applied during the last 50 ms of the life time of the mercury drop. The current is measured twice during the life time of each drop, firstly just before the pulse and second one just before the drop falls. The difference in the current is plotted resulting a peak shaped curve. The top of the peak corresponds to $E_{1/2}$ and the height of the peak depends on the concentration.

The peak current in differential pulse voltammetry increases linearly with the concentration of the analyte. It also increases with the pulse amplitude but in a complicated linear fashion. In practice amplitudes greater than 100 mv are not used, since the peaks broaden and the resolution is significantly inhibited.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Applied Potential program</th>
<th>Current response</th>
<th>Working electrode</th>
<th>LOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAST</td>
<td><img src="Image" alt="Graph of E vs. time" /></td>
<td><img src="Image" alt="Graph of I vs. E" /></td>
<td>DME</td>
<td>$10^{-6}$ M</td>
</tr>
<tr>
<td>NPP (NPV)</td>
<td><img src="Image" alt="Graph of E vs. time" /></td>
<td><img src="Image" alt="Graph of I vs. E" /></td>
<td>DME (HMDE)</td>
<td>$10^{-7}$ M (-$10^{-8}$ M)</td>
</tr>
<tr>
<td>SCV</td>
<td><img src="Image" alt="Graph of E vs. time" /></td>
<td><img src="Image" alt="Graph of I vs. E" /></td>
<td>(HMDE)</td>
<td>$10^{-1}$ M</td>
</tr>
<tr>
<td>DPP (DPV)</td>
<td><img src="Image" alt="Graph of E vs. time" /></td>
<td><img src="Image" alt="Graph of I vs. E" /></td>
<td>DME (HMDE)</td>
<td>$10^{-7}$ M</td>
</tr>
<tr>
<td>SWP (SWV)</td>
<td><img src="Image" alt="Graph of E vs. time" /></td>
<td><img src="Image" alt="Graph of I vs. E" /></td>
<td>DME (HMDE)</td>
<td>$10^{-6}$ M</td>
</tr>
<tr>
<td>ACP (ACV)</td>
<td><img src="Image" alt="Graph of E vs. time" /></td>
<td><img src="Image" alt="Graph of I vs. E" /></td>
<td>DME (HMDE)</td>
<td>$10^{-7}$ M</td>
</tr>
</tbody>
</table>

Fig. 7.6: Some basic parameters in different voltammetric/polarographic techniques
The higher detection limit in this technique is due to superior discrimination against charging current and impurity Faradaic current.

The peak current in differential pulse polarography is given by

$$i_p = \frac{n^2 F^2}{4RT} A C_a \Delta E_A \sqrt{\frac{D}{\pi \tau_p}}$$  \hspace{1cm} \text{... (7.3)}

where, $i_p =$ Peak current, $n =$ Number of exchanged electrons, $F =$ Faraday constant, $R =$ Gas constant, $T =$ Temp. in Abs. Scale, $A =$ Electrode surface area, $C_a =$ Concentration of the analyte, $\Delta E_A =$ Pulse amplitude, $D =$ Diffusion coefficient of the analyte, and $\tau_p =$ Pulse duration.

The detection limit for the determination by this technique is similar to square wave polarography at $10^{-7} - 10^{-8}$ mol/dm$^3$. But for irreversible reaction it is lowered.

### 7.5.3 Square Wave Polarography/Voltammetry

This is a type of pulse polarography that offers the advantages of high sensitivity, great speed and low detection limit. The entire voltammogram is obtained in less than 10 ms. It uses a potential wave form similar to one used in DPP and the entire potential sequence is applied during the life time of a single drop. This can be used with DME and HMDE. The excitation signal in this technique is obtained by superimposing the pulse shown on to the stair case signal. The length of each step in stair case signal is synchronized with the pulse period ($\tau$) and is about 5 ms. The potential step is 10 mv ($\Delta E_s$). The magnitude of the pulse is often 50 mv. Under these conditions corresponding to a pulse frequency of 200 Hz, a 1-V scan require 0.5 s.

For reversible reactions, a larger pulse is used so that its size is great enough for the oxidation of the product formed in the forward reaction occurs during the reverse phase. The forward pulse gives the cathodic current $i_1$, while the reverse phase gives the anodic current $i_2$ and the difference between these two $\Delta i = i_2 - i_1$ is plotted to give the voltammograms. This difference is directly proportional to the concentration, the potential at the peak corresponds to the $E_{1/2}$. It is possible to increase the precision of
the analysis by signal averaging data from several voltammetric scans. Detection limits for square wave voltammetry are reported to be $10^{-7}$ to $10^{-8}$ M.

The peak current in this technique is given by

$$i_p = kn^2 \frac{\sqrt{D/\Delta E_A}}{C_a}$$ … (7.4)

where, $i_p$ = peak current, $k$ = constant, $n$ = number of exchanged electrons, $D$ = diffusion coefficient of analyte, $\Delta E_A$ = Pulse amplitude, and $C_a$ = concentration of the analyte.

**SAQ 4**

i) Distinguish between
   a) Linear-scan polarography and pulse polarography.
   b) Differential-pulse polarography and square-wave polarography.

ii) Which one is better and why? NPP(NPV) or DPP(DPV) ?

**7.5.4 Cyclic Voltammetry**

Cyclic Voltammetry (CV) is an attractive method for the teaching of a number of concepts in electrochemistry. In brief, it is perhaps the most versatile electrochemical technique for the study of electroactive species. The effectiveness of CV results from its capability for rapidly observing the redox behaviour over a wide range of potential. The resulting voltammogram is similar to a conventional spectrum in that it conveys information as a function of an energy scan. In spite of its wide applications, this technique is not generally well understood as compared to other instrumental techniques such as spectroscopy and chromatography.

![Fig. 7.8: Typical cyclic voltammogram](image)

**Fundamentals of Cyclic Voltammetry:** It consists of cycling the potential of an electrode that is immersed in an unstirred solution of the electroactive species and then measuring the resulting current. The potential of this working electrode is controlled versus a reference electrode such as a saturated calomel electrode (SCE) or a
silver/silver chloride electrode (Ag/AgCl). The controlling potential which is applied across these two electrodes can be considered as excitation signal. The excitation signal for CV is a linear potential scan with a triangular waveform as given in Fig. 7.9. This triangular potential excitation signal sweeps the potential of the electrode between two values, sometimes called the switching potentials. The excitation signal in Fig. 7.9 causes the potential first to scan negatively from +0.80 (initial potential) to –0.20 V ($E_f$ final potential) versus SCE at which point the scan direction is reversed, resulting a positive scan back to the original potential of +0.80 V ($E_i$). The scan rate as reflected by the slope is 50 mV per second as shown in Fig. 7.9. A second cycle is indicated by the darkened line. Single or multiple cycles can be used.

A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the response signal to the potential excitation signal. The voltammogram is a display of current (vertical axis) versus potential (horizontal axis). Since the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. This will be helpful in understanding the basic principle of the technique.

A typical cyclic voltammogram is given in Fig. 7.10. In a platinum working electrode is a solution containing 6.0 mm of $K_3Fe(CN)_6$ as the electroactive species in 1.0 M KNO$_3$ in water as the supporting electrolyte. The potential excitation signal used to
obtain this voltammogram is shown in Fig. 7.9 but with the negative switching potential of ~0.15V. Thus, the vertical axis in Fig.7.9 is now the horizontal axis of Fig.7.10. The initial potential \( E_0 \) of 0.80 V applied at (a) is chosen to avoid any electrolysis of \([\text{Fe(CN)}_6]^{3-}\) when the electrode is switched on. The potential is then scanned negatively, forward scan, as indicated by the arrow. When the potential is sufficiently negative to reduce \([\text{Fe}^{III}(\text{CN})_6]^{3-}\), the anodic current rapidly increases until the concentration of \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) at the electrode surface is substantially diminished, resulting the current to peak (d).

The cathodic current increases rapidly (b → d) until the concentration of \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) at the electrode surface is substantially diminished, resulting the current to peak (d). The current then decays (d → g) as the solution surrounding the electrode is depleted of \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) due to electrolytic conversion to \([\text{Fe}^{II}(\text{CN})_6]^{4+}\). The scan direction is then switched to positive at ~0.15 V (t) for the reverse scan. The potential is still sufficiently negative to reduce \([\text{Fe}^{III}(\text{CN})_6]^{3-}\), so the cathodic current continues even though the potential is now scanning in the positive direction. When the electrode becomes sufficiently strong oxidant, \([\text{Fe}^{II}(\text{CN})_6]^{3-}\), which has been accumulating adjacent to the working electrode, can now be oxidized by the electrode process:

\[
[\text{Fe}^{III}(\text{CN})_6]^{3-} + e \rightarrow [\text{Fe}^{II}(\text{CN})_6]^{4+} \quad \ldots (7.5)
\]

The electrode is now sufficiently strong reductant to reduce \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) to \([\text{Fe}^{II}(\text{CN})_6]^{4+}\).

This causes anodic current (i → k). The anodic current rapidly increases until the surface concentration of \([\text{Fe}^{II}(\text{CN})_6]^{4+}\) is diminished, resulting the current to peak (j). The current then decays (j → k) as the solution around the electrode is depleted of \([\text{Fe}^{II}(\text{CN})_6]^{4+}\). The first cycle is completed when the potential reaches back to + 0.80 V. Now the cyclic voltammogram is obtained. It is clear that any potential positive of ~0.40 V would be suitable as the initial potential in the reduction of \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) would not occur when the potential is applied. This procedure avoids inadvertent electrolysis as a result of applying the initial potential. In the forward scan \([\text{Fe}^{II}(\text{CN})_6]^{4+}\) is electrochemically generated from \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) as indicated by the cathodic current while in the reverse scan \([\text{Fe}^{II}(\text{CN})_6]^{4+}\) is oxidized back to \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) as indicated by the anodic current. A more detailed understanding can be obtained by considering the Nernst equation and the changes in concentration that occur in solution adjacent to the electrode during electrolysis. The potential excitation signal depends on the ratio of \([\text{Fe}^{III}(\text{CN})_6]^{3-}/[\text{Fe}^{II}(\text{CN})_6]^{4+}\) at the electrode surface as described by Nernst equation for a reversible system:

\[
E = E^\circ + \frac{0.0595}{1} \log \frac{[\text{Fe}^{III}(\text{CN})_6]^{3-}}{[\text{Fe}^{II}(\text{CN})_6]^{4+}} \quad \ldots (7.7)
\]

where \(E^\circ\) is the formal reduction potential of the sample. An initial value of \(E\) which is sufficiently positive of \(E^\circ\) maintains a ratio in which \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) greatly predominates. Thus, application of +0.80 V at the initial potential causes negligible current. However, as \(E\) is scanned negatively, conversion of \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) to \([\text{Fe}^{II}(\text{CN})_6]^{4+}\) by reduction is mandatory for satisfaction of the Nernst equation. The ratio of iron redox states that must exist at the electrode surface at several potentials during the scan is shown on the lower horizontal axis in Fig.7.10. The logarithmic relationship between \(E\) and \([\text{Fe}^{III}(\text{CN})_6]^{3-}/[\text{Fe}^{II}(\text{CN})_6]^{4+}\) is reflected by a rapid rate of change in the region where \(E = E^\circ\) i.e., \([\text{Fe}^{III}(\text{CN})_6]^{3-}/[\text{Fe}^{II}(\text{CN})_6]^{4+} = 1\). This causes the diametric rise in cathodic current (b → d) during the forward scan.

The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current \((I_{pa})\) and cathodic peak current \((I_{pc})\), and anodic peak potential \((E_{pa})\).
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and cathodic peak potential \( (E_{pc}) \). These parameters are labeled in Fig.7.10. One method of measuring \( I_p \) involves extrapolation of a baseline current as shown in Fig.7.10. The establishment of correct baseline is essential for the accurate measurement of peak currents. It is generally difficult for more complicated systems. The peak current for a reversible system is described by the Randles-Sevcik equation for the forward sweep of the first cycle.

\[
i_p = (2.686 \times 10^5) n^{3/2} AD^{1/2} C_0 v^{1/2}
\]

where \( i_p \) is peak current in ampere, \( n \) is electron stoichiometry, \( A \) is area of the electrode (cm\(^2\)), \( D \) is diffusion coefficient (cm\(^2\)/second), \( C_0 \) is the concentration (mol/cm\(^3\)), and \( v \) is scan rate (v/second)

\( i_p \propto C_0 \) if all the parameters are kept constant. The relationship to concentration is particularly important in analytical applications and in studies of electrode mechanism. The value of \( I_{pa} \) and \( I_{pc} \) should be identical for a simple reversible (fast) couple i.e.

\[
\frac{I_{pc}}{I_{pa}} = 1
\]

According to Eq. (7.8), \( I_p \) increases with \( v^{1/2} \). However, the ratio of peak currents can be significantly affected by chemical reactions coupled to the electrode process. A redox couple in which both species rapidly exchange electrons with the working electrode is called an electrochemically reversible couple. The formal reduction potential \( (E'_0) \) for a reversible couple is centered between \( E_{pa} \) and \( E_{pc} \).

\[
E'_0 = \frac{E_{pa} + E_{pc}}{2}
\]

The number of electrons transferred in the electrode reaction \( (n) \) for a reversible couple can be determined from the separation between peak potentials.

\[
\Delta E_p = \frac{E_{pa} - E_{pc}}{n} = \frac{0.059}{n}
\]

Thus, for a one-electron process, such as the reduction of \([\text{Fe}^{3+}\text{(CN)}_6]^{3-}\) to \([\text{Fe}^{2+}\text{(CN)}_6]^{4-}\), exhibited \( \Delta E_p \) of 0.059 V. Slow electron transfer at the electrode surface, “irreversibility” causes the peak separation \( (\Delta E) \) to increase.

The electrochemical irreversibility is caused by slow electron exchange of the redox species with the working electrode. In this case Eqs. (7.8), (7.9), (7.10) and (7.11) are not applicable. The electrochemical irreversibility is characterized by a separation of peak potential greater than indicated by Eq. (7.11).

The electrochemical irreversibility is caused by slow electron exchange of the redox species with the working electrode. The process is said to be quasi-reversible if it is reversible at low sweep rates but becomes irreversible at higher ones after having passed through a region known as quasi-reversible at intermediate values. This transition from reversibility occurs when the relative rate of electron transfer with respect to that of mass transport is insufficient to maintain Nernstian equilibrium at the electrode surface. In the quasi-reversible region, both forward and backward reactions make a contribution to the observed current.

Peak separation greater than the predicted theoretical value \( (59/n \text{ mV}) \) is typically caused by IR drop due to high resistance between working and reference electrodes. This is especially a problem at fast scan rates where ‘\( I \)’ can be large and in non-
aqueous solvent where ‘R’ can be large. Also, slow heterogeneous electron exchange with the electrode can increase $E_p$.

The various criteria applied for the diagnosis of reversibility, irreversibility or quasi-reversibility are summarized in Table 7.1.

**Table 7.1: Diagnostic test to decide the reversibility of a redox reaction by cyclic voltammetry**

<table>
<thead>
<tr>
<th>Criteria for reversible system</th>
<th>Criteria for quasi-reversible system</th>
<th>Criteria for total irreversible system</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) $E = E_p$ - $E_{pc}$ = (0.0591/n) V</td>
<td>(i) $I_p$ increases with $v^{1/2}$ but is not proportional to it.</td>
<td>(i) No reverse peak.</td>
</tr>
<tr>
<td>(ii) $[E_p - E_{p/2}] = (0.0591/n)$ V</td>
<td>(ii) $[I_p / I_{pc}] = 1$ provided $\alpha_c = \alpha_a = 0.5^*$.</td>
<td>(ii) $I_{pc} \propto v^{1/2}$</td>
</tr>
<tr>
<td>(iii) $[I_{pa} / I_{pc}] = 1$</td>
<td>(iii) $E_p$ is greater than 0.059/n V and increases with increasing $v$.</td>
<td>(iii) $E_{pc}$ shift -30/$\alpha_c n_\alpha$ * mV for each decade increase in $v$.</td>
</tr>
<tr>
<td>(iv) $I_p \propto v^{1/2}$</td>
<td>(iv) $E_{pc}$ shifts negatively with increasing $v$.</td>
<td>(iv) $(E_p - E_{p/2}) = 48/\alpha_c n_\alpha$ mV.</td>
</tr>
<tr>
<td>(v) $E_p$ is dependent of $v$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(vi) At potential beyond $E_p$, $I^{-2} \propto$ time.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The notations have their usual meaning as described in the text

$\alpha_c$ and $\alpha_a$ are transport numbers of cation and anion respectively

$n_\alpha$ is the number of electrons transferred upto, and including, the rate determining step

Probably the most marked feature of a cyclic voltammogram of a total irreversible system is the total absence of a reverse peak. However, such a feature on its own does not necessarily imply an irreversible electron transfer process, but could be due to a fast following chemical reaction. Hence, other tests must therefore be made.

In some cases, the anodic current is low as compared to the cathodic current. This is because throughout most of the experiment there is a concentration difference which drives back the reduced species away from the electrode, most of the reduced species produced in forward reduction process, therefore, diffuse into the bulk solution and cannot be re-oxidized on the time scale of a cyclic voltammetric experiment during reverse direction, *i.e.* anodic process. Hence, it gives reduced anodic peak current as compared to cathodic peak current.

**Instrumentation**

Cyclic voltammetry requires a waveform generator to produce the excitation signal, a potentiostat to apply this signal to an electrochemical cell, similar to a polarographic cell, a current to voltage converter to measure the resulting current and an X-Y recorder or oscilloscope to display the voltammogram. The first three items are normally incorporated into a single electronic device, though modular instruments
may also be used. The potentiostat ensures that the working electrode potential will not be influenced by the reactions which take place. Data may be obtained with X-Y recorder at slow scan i.e. less than 500 mV/second while storage oscilloscope at faster rates having scan rate upto 20,000 V/second have been used, however ratio faster than 100 V/second are rarely practical because of IR Drop and changing current.

Modern potentiostat utilize a three-electrode system as shown in Fig.7.11. The potentiostat applies the desired potential between a working electrode and a reference electrode. The working electrode is the electrode on which the electrolysis of interest takes place. The current required to sustain the electrolysis at the working electrode is provided with the help of an auxiliary electrode. This arrangement prevents large current from passing through the reference electrode that could change its potential. A normal polarographic cell may be used in this technique. Such cells usually consist of glass container with a cap having holes for introducing electrodes and for the passage of pure nitrogen gas for the removal of oxygen from the test solution similar to polarography. The reference electrode is typically a SCE in a Ag/AgCl electrode which is often isolated from the solution with a salt bridge to prevent contamination by leakage from the reference electrode. The auxiliary electrode is usually a platinum wire that is placed directly into the solution. Since the limiting (peak) current in all the voltammetric techniques is temperature dependent, the cell should be thermostated. Cells are commercially available that may require as little as 1-2 ml of the test solution. Thin-layer cells enable voltammograms to be recorded on down to 60 µl.

A large variety of working electrodes have been used in voltammetry. The dropping mercury electrode is used especially in polarography and the hanging mercury drop electrode (HMDE) in cyclic voltammetry. A thin coat of mercury can be deposited on a substrate such as graphite to form a mercury film electrode (MFE). A significant advantage of mercury is its good negative potential range. Solid electrode such as platinum, gold, glossy carbon, wax impregnated graphite and carbon-paste are also used in cyclic voltammetry. Such electrodes have a better positive potential range than mercury.

In conclusion CV has become increasingly popular in all fields of chemistry as a means of studying of redox states. The technique enables a wide potential range to be scanned rapidly for reducible or oxidizable substances. This capability together with its variable time scale and good sensitivity make this the most versatile electrochemical technique. At the same time it must be emphasized that its merits are mainly in the realm of qualitative or diagnostic purpose. Quantitative measurements (rate or concentration) are best obtained via other techniques e.g. pulse technique. Due to the kinetic control of many cyclic voltammetry experiments, some caution is advisable when evaluating the results in term of thermodynamic parameters like measurements of $E^\circ$.
SAQ 5

i) How are pulse methods better than the direct methods?

ii) What is the difference between voltammetry and polarography?

iii) What is the advantage of solid electrode (like platinum) over mercury electrode in CV?

iv) Why CV has been recognized as the most versatile electrochemical technique?

v) In a system that uses a three electrode potentiostat, between which two electrode is the potential measured?

7.6 STRIPPING METHODS

Stripping voltammetry is the most sensitive electrochemical technique for the quantitative analysis of microquantitative electroactive analytes which oxidize or reduce reversibly at solid electrodes or form insoluble species at the electrode surface that can be subsequently removed electrochemically and analysed.

Basically two steps are involved in this technique

1. The analyte of interest is electrolytically deposited on the working electrode by controlled potential electrolysis.
2. A reverse potential seal or stripping step is applied in which the deposited analyte is removed from the electrode.

The first step is basically preconcentration or electrodeposition while the second one is the stripping step. Three different types of this technique are available.

7.6.1 Anodic Stripping Voltammetry

This technique is used to determine trace amounts of metal ions that can be preconcentrated at an electrode by reduction to the metallic state. The microelectrode behaves as a cathode during the deposition step and as an anode during the stripping step with the analyte being oxidized to the original form:

This may be explained in detail taking the example of Cu²⁺, the deposition reaction at HMDE (Hanging Mercury Drop Electrode) held at a cathodic potential sufficient to deposit the metal ion on the electrode

\[ \text{Cu}^{2+} \text{(aq)} + 2e^- = \text{Cu(Hg)} \]  \hspace{1cm} \text{... (7.12)}
where Cu(Hg) is copper amalgamated with mercury. This step is basically a preconcentration step where the metal ion from a large volume of the solution is concentrated on a small volume of the electrode. The solution is stirred during the electrolysis to increase the rate of deposition. Near the end of the deposition time stirring is stopped and usually 1-30 mins are used for deposition. In the second step, the potential is scanned anodically towards more positive potential. When the potential becomes positive, the analyte is stripped from the electrode returning to its oxidized form

\[ \text{Cu (Hg)} = \text{Cu}^{2+} (aq) + 2e^- \]  \hfill (7.13)

And the current during this step is monitored as a function of potential giving rise to the voltammogram, the peak current of which is proportional to the analyte concentration in the solution. This technique is sensitive to experimental conditions like area of mercury film electrode or size of the Hg drop, deposition time, rest time, rate of stirring and scan rate during the stripping step. If properly controlled this method will be quite sensitive and accurate and is best used for metals that form amalgams.

**Stripping voltammetry:**
A voltammetric technique in which the analyte is first deposited on the electrode from a large volume of the analyte and then stripped electrochemically monitoring the current as a function of the potential.

**Fig. 7.12: Details of stripping voltammetry**
In anodic stripping voltammetry the determination of the analyte is based on the anodic dissolution. This process is followed voltammetrically and the peak current thus obtained is proportional to the potential scan rate and radius of mercury drop (HMDE) or scan rate and surface area of the mercury film (TMFE). In both the cases the peak current \( i_p \) is given by

\[
i_p = K \cdot n^{3/2} \cdot D^{1/2} \cdot c_M^0 \cdot (\text{Hg})^{n^{1/2} \cdot r^2 \cdot J_{\text{ace}}}
\]

\[
i_p = K \cdot n^{2} \cdot A_p \cdot c_M^0 \cdot (\text{Hg}) \cdot \nu \cdot t_{\text{ace}}
\]

Where, \( i_p \) = peak current, \( n \) = electron transfer during the oxidation of the analyte, \( D \) = diffusion coefficient, \( K \) = constant, \( C_M \) = concentration of metal in the amalgam, \( A_p \) = surface area, \( \nu \) = scan rate, and \( t_{\text{ace}} \) = accumulation time.

However in both the cases the peak current depends on the accumulation time \( t_{\text{ace}} \) and therefore, is proportional to the concentration of analyte \( c_M^0 \) (Hg) in the amalgam and indirectly proportional to the concentration of the analyte in the sample solution.

Peak currents in this technique are a linear function of concentration and hence this technique can be used for the determination of many metal ions in trace quantities in environmental samples.

### 7.6.2 Cathodic Stripping Voltammetry

It is used for the determination of anions that form insoluble mercury (I) salts at the mercury surface or insoluble silver salts on a silver electrode. The experimental design is similar to that for A.S.V. with two modifications. The decomposition step involves the oxidation of the Hg electrode to Hg\(^{2+}\) which then reacts with the analyte to form an insoluble film at the surface. The decomposition step with Cl\(^-\)

\[
2\text{Hg}(l) + 2\text{Cl}^- (\text{aq}) = \text{Hg}_2\text{Cl}_2(s) + 2\text{e}^- \quad \ldots \quad (7.15)
\]

The second step, i.e. stripping, is followed by scanning cathodically towards a more negative potential reducing Hg\(^{2+}\) back to Hg and returning the analyte to the solution.

\[
\text{Hg}_2\text{Cl}_2(s) + 2\text{e}^- = 2\text{Hg}(l) + 2\text{Cl}^- (\text{aq}) \quad \ldots \quad (7.16)
\]

(Some analytes analysed are halides, sulphides, mercaptan.)

### 7.6.3 Adsorptive Stripping Voltammetry

In this technique analyte is adsorbed on the electrode surface and there is no electrolysis step and after complete deposition the potential is scanned in anodic or cathodic direction depending on whether the analyte is to be oxidized or reduced.

The deposition step in this method amounts to an electrochemical pre-concentration of the analyte, i.e. the concentration of the analyte on the surface of the microelectrode is greater than the bulk of solution and hence these methods are extremely sensitive and the detection limit can be improved by factors of \(10^6\) for selected species. Some analytes analysed by this method are cocaine and testosterone.

### SAQ 6

i) Which of the following is better and why?

a) Linear sweep voltammetry and cyclic voltammetry.

b) Anodic stripping voltammetry and Adsorptive stripping voltammetry.

...........................................................................................................................................
...........................................................................................................................................
ii) What are the two basic steps involved in stripping voltammetry?

iii) What is so special about the peak currents in Anodic stripping voltammetry?

### 7.7 ALTERNATING CURRENT METHODS

In this technique the linear potential is modulated by a sine wave voltage of a small amplitude. This produces an alternate current, whose size is determined by the direct potential applied and which is greatest at the half wave potential. The plot of selectively measured AC against the potential gives a peak shaped alternative current polarogram as shown in Fig.7.13.

![Fig. 7.13: Principle of AC voltammetry](image)

A simplified expression for peak current

\[ i_p = K n^2 E_a f^2 c_a \]  \hspace{1cm} (7.17)

where, \( i_p \) = peak current, \( K \) = constant, \( E_a \) = amplitude of superimposed AC, \( c_a \) = concentration of the analyte, \( n \) = number of electrons, and \( F \) = frequency

Thus, the height of AC polarographic peak can be used to determine the concentration in a way similar to DC polarographic method. AC polarographic peak currents are widely dependent on the kinetics of charge transfer reaction and the signals of strongly irreversible processes are suppressed. For reversible processes the half width of the peak \( b_n = \frac{90}{n} \text{(mv)} \) depends on the electron exchange as a result of which, for large value of \( n \), \( b \) will be narrower and with slow processes, \( b \) will be broader.
AC polarographic determinations are limited to a sensitivity of about $10^{-5}$ mol/dm$^3$ because of high capacitance current contribution which is the main source for periodic charging and discharging of double layer.

The above sensitivity for reversible redox processes can be improved to about $(5-10)^{-7}$ mol/dm$^3$ if the AC is measured at a particular phase shift with reference to the excitation signal in order to separate the Faradaic and capacitive current. This is the 1$^{st}$ harmonic AC polarography (AC-1, polarography). The measurement of the harmonic of the AC resulting from the nonlinearity of the Faradaic resistance, e.g. 2$^{nd}$ harmonic with the aid of phase selective rectification (AC - 2 polarography) reduces the capacitance current contribution thus increasing the sensitivity and the selectivity of the determination. The market available instruments are equipped to measure both the types of currents.

**SAQ 7**

How can the height of AC polarographic peak be utilized?

........................................................................................................................................................................................

........................................................................................................................................................................................

........................................................................................................................................................................................

7.7.1 **Voltammetry – Instrument**

The basic instrument consist of two important components

![Fig 7.14: Basic instrument for voltammetry](image)

1. Normal three electrode polarograph.
2. Linear scan voltage generator to give different type of signals.

The polarographic cell is made up of a three electrodes dipped in a solution containing the electroactive species and excess of inert electrolyte usually called supporting electrolyte.

i) **Working electrode**, usually a microelectrode whose potential is varied linearly with time.
ii) **Reference electrode**: Normally a standard electrode is used whose potential is constant throughout the experiment (saturated calomel electrode or Ag/AgCl electrode).

iii) **Counter electrode**, which is a coil of platinum wire or a pool of mercury that simply serves to conduct electricity from the signal source through the solution to the microelectrode.

The potentiostat allow to impose the potential scanning between the working and reference electrodes while the current flowing through the circuit is recorded between the working and auxiliary electrodes.

The computer CVA Trace analyzer from Metrohm Ltd. can be used as an integrated instrument with keyboard or a commercially available personal computer interface to measuring system with software can be used:

i) to send the scanning parameters to the potentiostatic analyzer and check its correctness and accuracy,

ii) handle the current potential output data.

### 7.8 SUMMARY

In this unit, you learnt about voltammetry. Various electrodes, especially the common microelectrodes used in voltammetry were discussed. Then we discussed the common voltammetry methods. The linear sweep voltammetry, sampled D.C. polarography and hydrodynamic voltammetry were discussed under the direct current methods. A detailed discussion of the different pulse methods was done including normal pulse voltammetry, differential pulse voltammetry, square wave voltammetry and cyclic voltammetry. Also you have learnt about the various stripping methods including anodic, cathodic and adsorptive stripping voltammetry. Alternating current methods were also discussed. In the last section of the unit we learnt about the instrumental details and steps involved in practical voltammetry.

### 7.9 TERMINAL QUESTIONS

1. Why is it not necessary to remove dissolved oxygen from the solution before recording voltammogram in case of anodic current?

2. Discuss the advantages and disadvantages of stripping techniques.

3. Why are the residual currents less with current sampled polarography?

4. Indium and Cadmium ions in 0.1 M HCl give peaks at potentials – 0.557 V and – 0.597 V by differential pulse polarographic analysis. When a standard solution containing 0.4 ppm of indium is analysed, it gave peak current (in arbitrary units) corresponding to 100.25 at – 0.557 V and 43.75 at – 0.597 V. A standard solution containing 0.4 ppm of Cd gave \( i_p \) 29.52 at – 0.557 V and 64.8 at – 0.597 V. What is the concentration of indium and cadmium in a sample if the peak current is 190 at \( \sigma \) 0.557 V and 120 at \( \sigma \) 0.597 V.

5. Anodic stripping voltammetry is used for the analysis of copper in a sea water sample using standard addition method. When a 50 ml sample is analysed it gave a peak current of 0.886 \( \mu \) A. A 5.00 \( \mu \) dm\(^3\) spike of 10 ppm Cu\(^{++}\) is added to the sample and the resulting peak current is 3.52 \( \mu \) A. Calculate the concentration of Cu\(^{++}\) in ppm in the given sample of sea water.

6. Suggest how Eq. (7.11) could be employed to determine the number of electrons \( n \) involved in a reversible reaction at a microelectrode.
7. Draw the DME and label its parts.

8. Why are stripping methods more sensitive than other voltammetric procedures?

9. What is the purpose of the electrodeposition step in stripping analysis?

10. How can the reversibility of an electrode process be investigated in cycle voltammetry?

11. Why must the electrode surface be regularly polished?

12. What is the equivalent equation for classical DC polarography?

13. What are the different pulse methods in voltammetry?

14. Why would the HMDE and the DME be unsuitable for use in flow systems?

15. What is usually meant by the terms anodic and cathodic and when is an electrode an anode or a cathode?

16. Why would an unstirred solution offer greater reproducibility?

17. Why can stripping voltammetry be applied to only a very small number of organic compounds?

18. What are the three most important roles played by the separation step?

### 7.10 ANSWERS

**Self Assessment Questions**

1. a) This is because in normal DC polarography, the electrode area is not constant.
   
   b) Tast polarography is also known as sampled DC polarography. In this technique instead of recording the current continuously, it is sampled for say a 5 millisecond period just before the drop falls. Between the sampling periods, the recorder is maintained at its last current level by means of a sample and hold circuit.

2. The major advantage of current sampling is that it substantially reduces large current fluctuations due to continuous growth and fall of the drops at dropping electrode.

3. a) Hydrodynamic voltammetry is the voltammetric method in which the current is measured as a function of the potential applied to a solid working electrode kept in stirring solution.
   
   b) In hydrodynamic voltammetry the flow of analyte solution may be done through a tube in which the microelectrode is fixed.
4. i) a)  

<table>
<thead>
<tr>
<th>Linear Scan Polarography</th>
<th>Pulse Polarography</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) In this technique, the potential of the working electrode is varied linearly as a function of time of the current response is recorded</td>
<td>i) The current is measured at a time when the difference between the Faradaic current of the interfering charging current is large</td>
</tr>
<tr>
<td>ii) Limited by charging current which is large initially in the drop life.</td>
<td>ii) The charging current is eliminated</td>
</tr>
<tr>
<td>iii) Slow, inconvenient apparatus &amp; poor detection limit</td>
<td>iii) Sensitivity improved by 6.5 times</td>
</tr>
</tbody>
</table>

b)  

<table>
<thead>
<tr>
<th>Differential Pulse Polarography</th>
<th>Square Wave Polarography</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) In this technique a 50 mv pulse is applied during the last 50ms of the life time of the mercury drop.</td>
<td>i) It uses a potential wave form similar to one used in DPP. The entire potential sequence is applied during the life time of a single drop.</td>
</tr>
<tr>
<td>ii) The peak current increases linearly with the concentration of the analyte.</td>
<td></td>
</tr>
</tbody>
</table>

ii) The differential pulse polarography is better than normal pulse polarography as a greater improvement is reached by using the programming wave. In this technique a 50 mV pulse is applied during the last 50 ms of the life time of the mercury drop. The current is measured twice during the life time of each drop, firstly just before the pulse and second one just before the drop falls. The difference in the current is plotted resulting a peak shaped curve. The top of the peak corresponds to $E_{1/2}$ and the height of the peak depends on the concentration.

5. i) The pulse methods are better than the direct methods as the sensitivity is improved by about 6.5 times by eliminating charging current. The current in these methods is measured at a time when the difference between the Faradaic current and the interfering charging current is large.

ii) Polarography is voltammetry at controlled potential using a DME as the working electrode.

iii) Solid electrode (like platinum) is advantageous over mercury electrode in CV as they have a better positive potential range than mercury.

iv) CV has become increasingly popular in all fields of chemistry as a means of studying of redox states. The technique enables a wide potential range to be scanned rapidly for reducible or oxidizable substances. This capability together with its variable time scale and good sensitivity make this the most versatile electrochemical technique.

v) The potential is measured between a working electrode and reference electrode.
6. i) a) The cyclic voltammetry is better than linear sweep voltammetry as CV has the capability for rapidly observing the redox behaviour over a wide range of potential. The resulting voltammogram is similar to a conventional spectrum in that it conveys information as a function of an energy scan.

b)  The Adsorptive stripping voltammetry is better than the Anodic stripping voltammetry. In Adsorptive stripping voltammetry technique analyte is adsorbed on the electrode surface and there is no electrolysis step and after complete deposition the potential is scanned in anodic or cathodic direction depending on whether the analyte is to be oxidized or reduced. The deposition step in this method amounts to an electrochemical pre-concentration of the analyte, i.e. the concentration of the analyte on the surface of the microelectrode is greater than the bulk of solution and hence these methods are extremely sensitive and the detection limit can be improved by factors of $10^6$ for selected species.

ii) The two basic steps involved in stripping voltammetry are

1. The analyte of interest is electrolytically deposited on the working electrode by controlled potential electrolysis.

2. A reverse potential seal or stripping step is applied in which the deposited analyte is removed from the electrode.

The first step is basically preconcentration or electrodeposition while the second one is the stripping step.

iii) In Anodic stripping voltammetry the peak current thus obtained is proportional to the potential scan rate and radius of mercury drop (HMDE) or scan rate and surface area of the mercury film (TMFE). In both the cases the peak current depends on the accumulation time $t_{acc}$ and, therefore, is proportional to the concentration of analyte $C_{M^+}(Hg)$ in the amalgam and indirectly proportional to the concentration of the analyte in the sample solution. Peak currents in this technique are a linear function of concentration and hence this technique can be used for the determination of many metal ions in trace quantities in environmental samples.

7. The height of AC polarographic peak can be used to determine the concentration in a way similar to DC polarographic method. AC polarographic peak currents are widely dependent on the kinetics of charge transfer reaction and the signals of strongly irreversible processes are suppressed. For reversible processes the half width of the peak $b_0 = \frac{90}{n} (mV)$ depends on the electron exchange as a result of which, for large value of $n$, $b$ will be narrower and with slow processes, $b$ will be broader.

Terminal Questions

1. $O_2$ interferes at zero potential and while scanning towards negative potential. If scanning is towards more positive potentials generating anodic current, dissolved oxygen will not interfere and hence need not be removed.

2. **Advantages of stripping techniques**: The sensitivity is more because of preconcentration step. **Disadvantages of stripping techniques**: These
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3. The residual currents are less with current sampled polarography as current is measured near the end of the drop.

4. Peak currents in differential pulse polarography are directly proportional to the analytes concentration

\[ i_p = k \text{ (analyte ppm)} \]

where \( k \) is a constant depending on the analyte and applied potential. The values of \( k \) at potentials \(-0.557\) \( (E_1) \) and \(-0.597\) \( (E_2) \) for both the metals are given by

\[ K_{In,E_1} = \frac{100.25}{0.4} = 250.62 \text{ ppm}^{-1} \]
\[ K_{In,E_2} = \frac{43.75}{0.4} = 109.4 \text{ ppm}^{-1} \]
\[ K_{Cd,E_1} = \frac{29.52}{0.4} = 73.8 \text{ ppm}^{-1} \]
\[ K_{Cd,E_2} = \frac{64.8}{0.4} = 162.0 \text{ ppm}^{-1} \]

Writing the simultaneous equations for the current at the two potentials

\[ iE_1 = 250.62 \text{ (Con In)} + 73.8 \text{ (Con Cd)} = 190 \]
\[ iE_2 = 109.4 \text{ (Con In)} + 162.0 \text{ (Con Cd)} = 120 \]

On solving these two equations we get the

\[ \text{Con In} = 0.674 \text{ ppm} \]
\[ \text{Con Cd} = 0.285 \text{ ppm} \]

in the given sample.

5. Peak current in anodic stripping voltammetry is proportional to the analyte concentration

\[ i_p \propto \text{Cu}^{2+} \text{ (ppm)} \]

\[ i_p = k \text{ (Con. Cu}^{2+}) \]

where \( k \) is a constant

Thus for the sample \( 0.886 = k \text{ (con. Cu}^{2+}) \) \( \ldots (1) \)

and for the standard solution

\[ 3.52 = k \left[ \frac{0.05 \text{dm}^3}{0.05 \text{dm}^3 + 5 \times 10^{-6} \text{dm}^3} (\text{Con. Cu}^{2+}) + \frac{5.00 \times 10^{-6} \text{dm}^3}{0.05 \text{dm}^3 + 5 \times 10^{-6} \text{dm}^3} (10 \text{ ppm}) \right] \ldots (2) \]

Solving the Eq. (1) for \( k \) and substituting in Eq. (2) the concentration of \( \text{Cu}^{2+} \) in the given sample of sea water comes out to \( 3.36 \times 10^{-4} \) ppm.

6. The number of electrons transferred in the electrode reaction \( (n) \) for a reversible couple can be determined from the separation between peak potentials.

\[ \Delta E_p = E_{p_a} - E_{p_c} = \frac{0.059}{n} \]

Thus, for a one-electron process such as the reduction of \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) to \([\text{Fe}^{II}(\text{CN})_6]^{4-}\) exhibits \( \Delta E_p \) of 0.059 V. So, by knowing \( \Delta E_p \) the number of
electrons \( n \) involved in a reversible reaction at a microelectrode can be determined.

7. Fig. 7.1 c

8. It is the most sensitive because it includes a preconcentration step in which the analyte is collected over a long period from a large volume and reoxidized (or re-reduced) in a short ‘burst’ creating an enhanced current signal.

9. The analyte of interest is electrolytically deposited on the working electrode by controlled potential electrolysis.

10. Refer to Table 7.1

11. Electrode products can often build up on the surface of a solid or stationary electrode. Species from the solution may adsorb on the surface. Some solid electrode materials may even develop oxide layers on the surface. All of these produce changes in the nature of the electrode and often completely distort the electrochemical response. By regular polishing back to a clean metal or graphite surface, some attempt can be made to achieve a reproducible surface. Better results are usually obtained from a smooth rather than a rough surface.

12. The Ilkovic equation: \( i_d = 708 \, nD^{1/2} \, m^{2/3} \, t^{1/6} \, c \)

13. Pulse methods
   i) Normal Pulse voltammetry
   ii) Differential Pulse voltammetry
   iii) Square wave voltammetry
   iv) Cyclic voltammetry

14. They are much too mechanically unstable. The drop can be knocked off far too easily. They have in fact been used in flow systems but great care and much patience is needed. Further it is difficult to construct very small cells to hold a mercury drop electrode – a major disadvantage.

15. An anodic reaction is an oxidation. A cathodic reaction is a reduction. An anode is an electrode at which an oxidation reaction is taking place. Its potential need not have a positive value but oxidation occurs more easily the more positive the potential. Thus, the anodic direction is to more positive potentials. Similarly a cathodic or reduction process could occur at a positive potential but as the electrode becomes more negative it becomes more cathodic.

16. Simple undisturbed diffusion is a highly reproducible phenomenon and highly suitable for an analytical application. In a stirred solution the movement of the solution can be highly complex and not always predictable. If eddies form in the stirred solution they are very unreproducible and must be avoided.

Even in a very evenly stirred solution a slight displacement of the electrode can change the flow pattern. Reproducible stirring requires careful cell design and experimentation. The best stirring is a rotating electrode in a reproducible position in the cell.
17. Most organic compounds do not form insoluble electrode products. Most organic compounds are soluble at these high dilution trace levels. Many of those organic electrode products that are insoluble cannot be reoxidised or reduced to form a stripping peak, or the insoluble layer is insufficiently coherent. The most common type of organic compound to which stripping analysis can be applied are those containing a thiol group.

18. i) To separate the analyte from a medium in which it cannot be determined.
   ii) To remove potential interfering species.
   iii) To separate and allow individual determination of electrochemically similar analytes.