POLAROGRAPHY

In 1922, Polarography was developed by (zech chemist, Jaroslav Heyrovsky , who won the noble prize for his discovery.

An electromechanical techniques of analysing solutions that measure the current flowing between two electrodes in the solution as well as gradually increasing applied well as gradually increasing applied voltage to determine respectively the concentration of a solute and its nature

Is a method of analysis in which the solution to be analysed is electrolysed in such a way that the graph of current against voltage shows what is in solution and how much is present.

In this method, a reference electrode and an indicator electrode are required.

Reference electrode - acts to maintain a constant potential throught the measurement.

Indicator electrode - acts to maintain a constant potential impressed upon it from an external source.

Advantages

- ✓ Surface area is reproducible
- ✓ Constant renewal of electrode surface eliminating poisoning effect
- ✓ Mercury forms amalgams with most metal ions and alkali metal ions which are reducible
- ✓ It is useful over the range of +0.4 to -1.8V

Disadvantages

- ✓ Electrodes cannot be used above +0.4V
- ✓ Capillary is difficult to maintain sice dust or either particularly matter can be block the capillary
- ✓ Mercury can be easily oxidixied thus limit the feasible range of the electrode

TYPES OF CUURRENT

RESIDUAL CURRENT

It is the sum of the relativity larger condens current (charging current) and a very small faradic current.

MIGRATION CURRENT

It is due to migration of cations from the bulk of the solution towards cathode due to diffusive force. Irrespective of concentration gradient

DIFFUSION CURRENT

Diffusion current is due to the actual diffusion of electroreducible ion from the bulk of the sample to the surface of the of the mercury droplets due to concentration gradient mercury droplets due to concentration gradient

LIMITING CURRENT

Beyond a certain potential , the current reach a steady value called as the limiting current

FACTOR AFFECTING DIFFUSION CURRENT

CONCENTRATION:

Diffusioncurrent is directly proportional to concentration of the electroreducible ions . This forms the basis quantitative analysis. i.e, if concentration is less , then diffusion current is less . If concentration is more then diffusion current also more

TEMPERATURE :

Diffusion of ions is being affected by temperature hence diffusion current also varies with respect is temperature (directly proportional)

ILKOVIC EQUATION

$$I_d = 708\ n\ C\ D\ 12\ m23\ t^{1}{}_{6}$$

I_d= diffusion current due to electro reducible ions.

n =no of electrons involved in the reduction of one molecule.

C =conc. Expressed in mmol/lit

D = wt .of mercury flowing through capillary

i = drop time in seconds.

APPLICATION

Qualitative analysis

- Direct comparison method.
- CCM- calibration curve method.
- Internal standard or pilot ion.
- Method of standard addition

Inorganic analysis

- composition of alloy.
- Purity of element.
- Analysis of trace trace elements like copper, Zn, iron, nickle, lead, manganese.
- Trace metals and metal containing drugs.
- Blood and serum cancer diagnosis