Unit III (C)

POLAROGRAPHY

Presented By

Mrs.G.Aruna

Department of Pharmaceutical Analysis
Krishna Teja Pharmacy college

Subject code: 15R00302 (Physical Pharmacy-I)

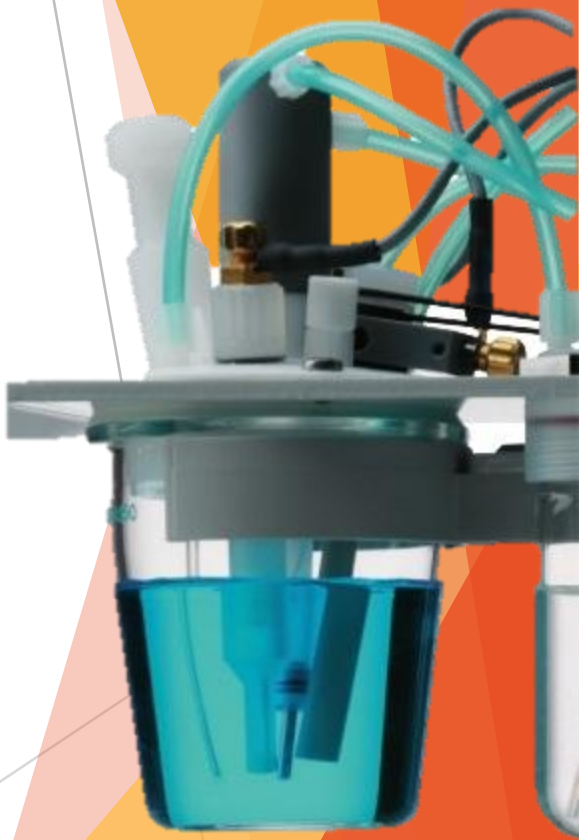
POLAROGRAPHY

- an electromechanical technique of analyzing solutions that measures the current flowing between two electrodes in the solution as well as the gradually increasing applied voltage to determine respectively the concentration of a solute and its nature.

-created by: Jaroslav Heyrovsky

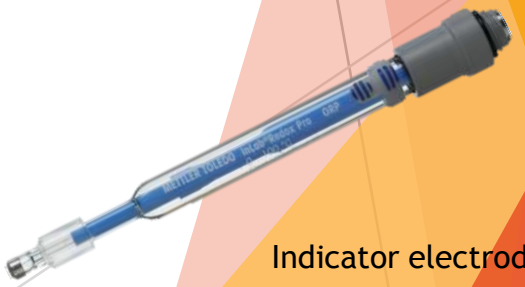
POLAROGRAPHY

- “Polarographic Analysis”
- Is a method of analysis based on the measurement of current electrolysis of an electroactive species at a given electrode potential under controlled conditions.
- It is the branch of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE), which are useful for their wide cathodic ranges and renewable surfaces.

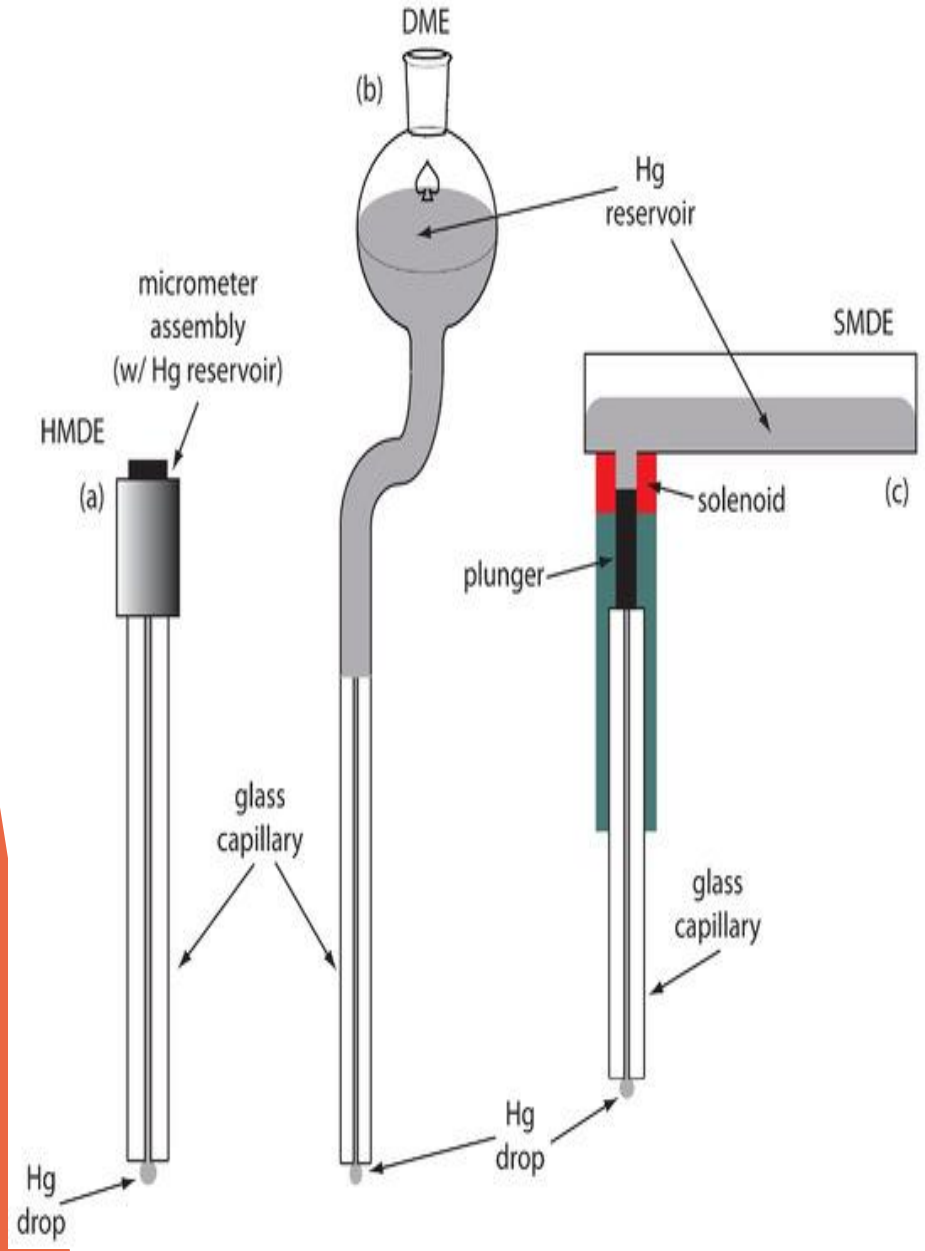


- In this method, a reference electrode and an indicator electrode are required.
- **Reference electrode-** acts to maintain a constant potential throughout the measurement.
- **Indicator electrode-** assumes the potential impressed upon it from an external source.

Reference electrode


Indicator electrode

EXAMPLES OF MERCURY ELECTRODES



In polarography, mercury is used as a working electrode, because mercury it is a liquid. The working electrode is often a drop suspended from the end of a capillary tube.

examples of electrodes:

1. HMDE (Hanging mercury drop electrode)-

we extrude the drop of Hg by rotating a micrometer screw that pushes the mercury from a reservoir through a narrow capillary.

2. DME (**dropping mercury electrode**)-

mercury drops form at the end of the capillary tube as a result of gravity. Unlike the HMDE, the mercury drop of a DME grows continuously—as mercury flows from the reservoir under the influence of gravity—and has a finite lifetime of several seconds. At the end of its lifetime the mercury drop is dislodged, either manually or on its own, and replaced by a new drop.

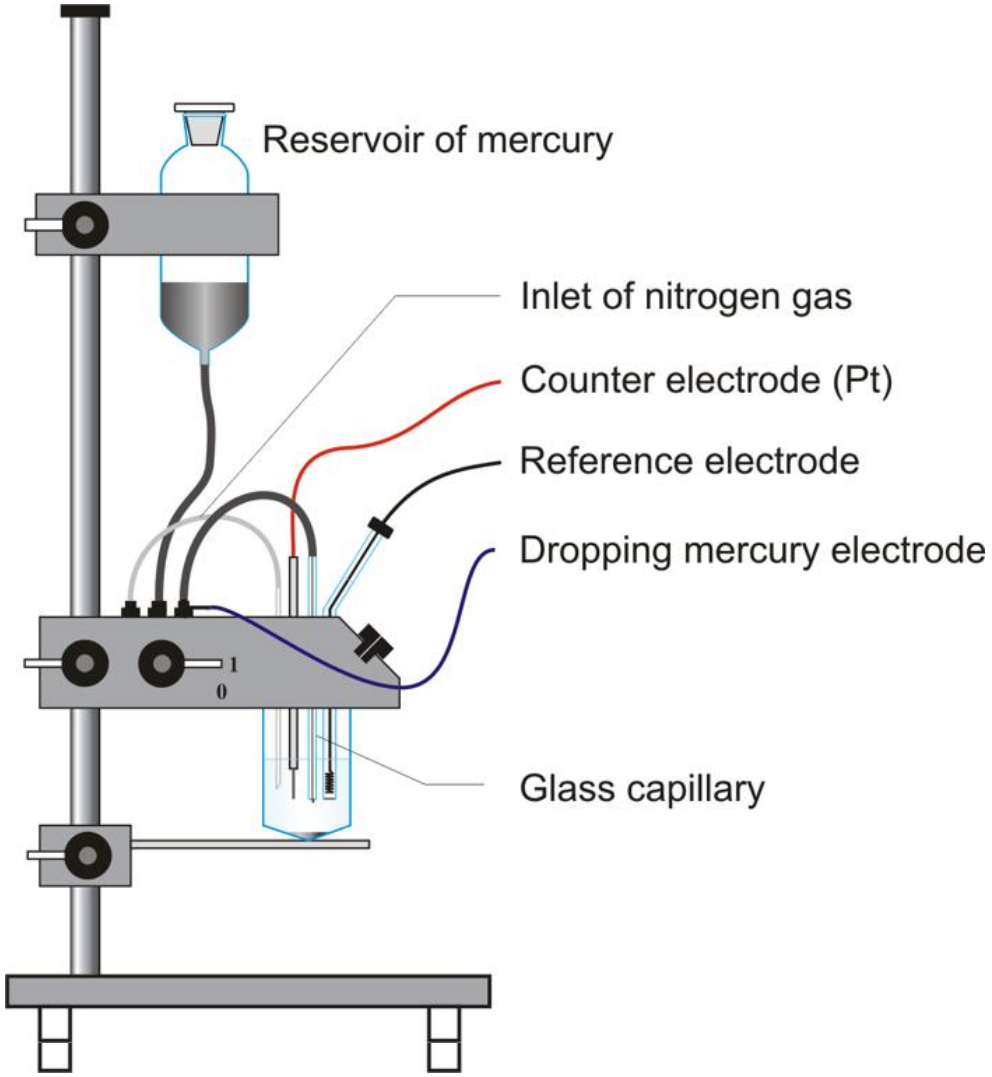
3. DSME (**static mercury drop electrode**)-

uses a solenoid driven plunger to control the flow of mercury. Activation of the solenoid momentarily lifts the plunger, allowing mercury to flow through the capillary and forming a single, hanging Hg drop.

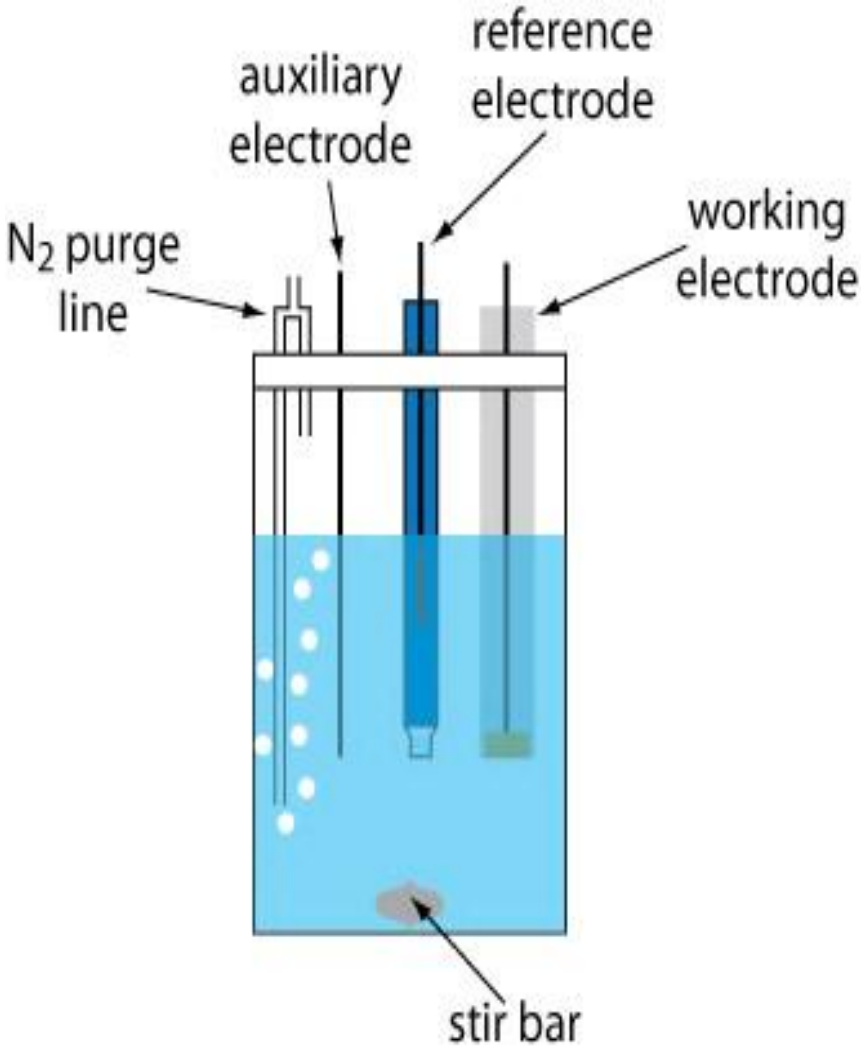
PRINCIPLE

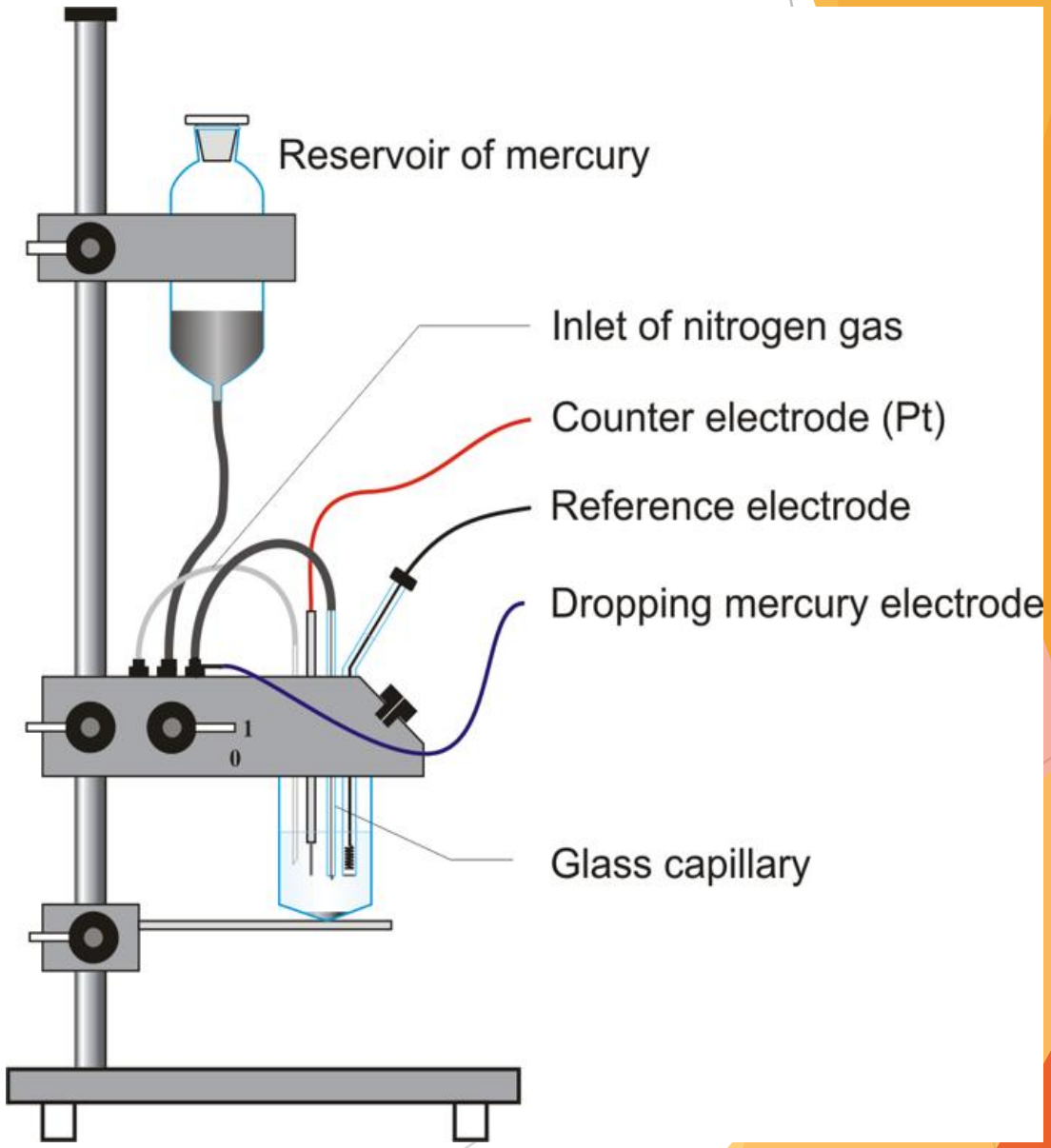
- Study of solutions or of electrode processes by means of electrolysis with two electrodes, one polarizable and one unpolarizable, the former formed by mercury regularly dropping from capillary tube.
  - **POLARIZED ELECTRODE**: Dropping Mercury Electrode (DME)
  - **DEPOLARIZED ELECTRODE**: Saturated Calomel Electrode

PRINCIPLE



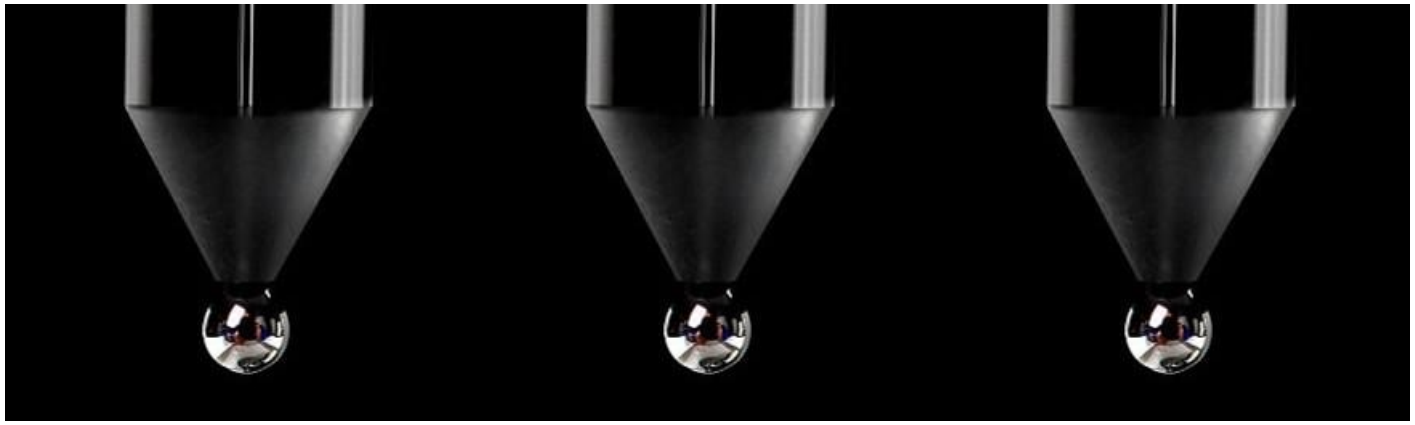
- **Mercury continuously drops from reservoir through a capillary tube into the solution.**
- **The optimum interval between drops for most analyses is between 2 and 5 seconds.**


reference electrode
auxiliary electrode
working electrode
N_2 purge line
stir bar


Reservoir of mercury
Inlet of nitrogen gas
Counter electrode (Pt)
Reference electrode
Dropping mercury electrode
Glass capillary

Why MERCURY?

- Mercury as working electrode is useful because:
  - It displays a wide negative potential range
  - Its surface is readily regenerated by producing a new drop or film
  - Many metal ions can be reversibly reduced into it.



POLAROGRAPHIC DATA

- Obtained from an automatic recording instrument is called a **polarogram**, and the trace is called a **polarographic wave.**

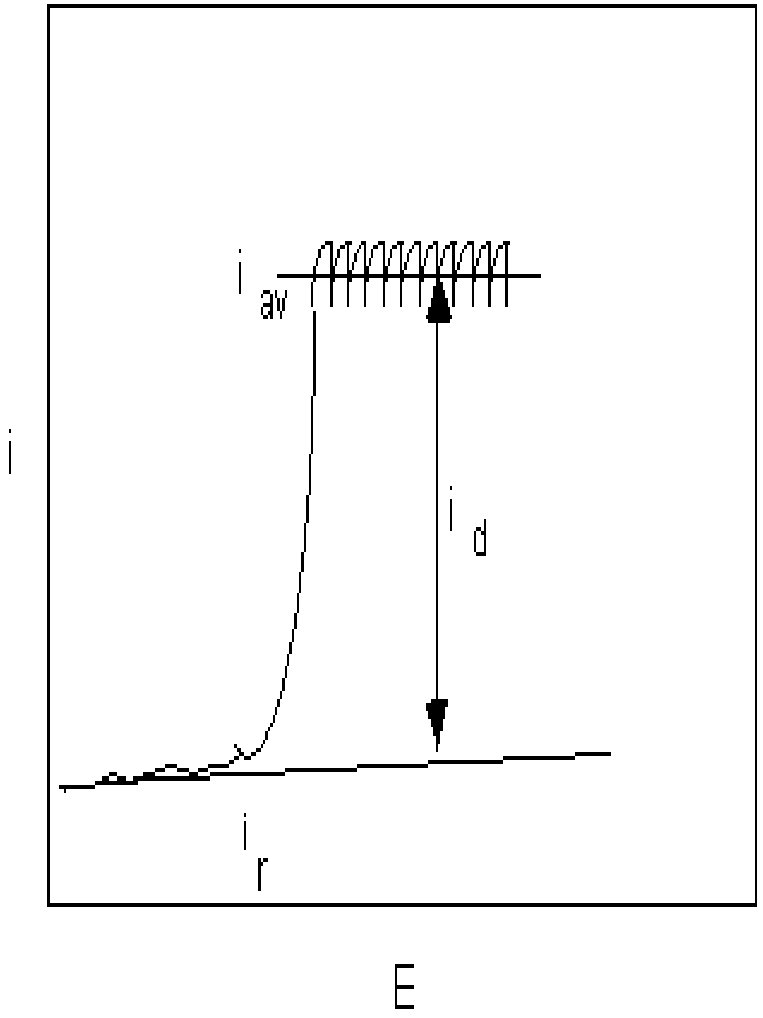
- **POLAROGRAM**
  - is a graph of current versus potential in a polarographic analysis.

  3 categories:

  A. collectively referred to as residual current
  B. referred to as diffusion current resulting from the reduction of the sample
  C. called the limiting current

❖ The diffusion current of a known concentration of reference standard are first determined followed by the determination of the diffusion current of the unknown concentration.

POLAROGRAM



- i_r (residual current) which is the current obtained when no electrochemical change takes place.
- i_{av} (average current/limiting current)is the current obtained by averaging current values throughout the life time of the drop while
- i_d (diffusion current) which is the current resulting from the diffusion of electroactive species to the drop surface.

Procedures

- Materials Required:

1. Polarographic Instrument.
2. Beaker.
3. 10 mL Pipette.
4. Wash bottle.
5. 100 mL volumetric flask.

Procedure

- **Reagents:**

1. 1, 2, 3, 4 and 5 mM Cadmium standards.
2. 2 M KCl solution.
3. 0.2% gelatin solution.
4. Distilled water.

Procedure

- Select the concentration from the list.
- Click “Load Cadmium Sample” button.
- Select “Scan Analysis”.
- Click “Plot Graph”.
- Select the unknown concentration from the concentration list.
- Repeat the steps 2, 3 and 4.
- Enter the concentration values on the worksheet.
- Plot calibration curve by clicking the “plot” button on the worksheet.
- Calculate the unknown concentration value from the calibration curve.

ADVANTAGES

1. Simple sample handling
2. Speed of analysis
3. High sensitivity
4. Comparable or better accuracy
5. Cheaper instrumentation and lower cost of chemicals used
6. Limited used of environmentally unfriendly organic solvents

Assay of Nitrofurantoin Oral Suspension

- Transfer an accurately measured volume of Nitrofurantoin Oral Suspension equivalent to about 50 mg of Nitrofurantoin to a 100 ml volumetric flask.
- Add 20 ml of dimethylformamide, agitate for 5 mins. add electrolyte solution to volume.
- Filter the solution discarding the first 25-30 ml of the filtrate.
- Pipet 3 ml of the clear filtrate into a 25ml volumetric flask
- Add 0.1 ml of gelatin solution to a polarographic cell that is impressed in a water bath regulated at 24.5 °C to 25.5 °C and deaerate by bubbling purified nitrogen through the solution for 10 mins.

- Insert the mercury electrode of a suitable polarography and record the polarogram using a standard calomel electrode as the reference electrode.
- Determine the height of the diffusion current at -0.0 V.
- Calculate the quantity in mg of Nitrofurantoin in each ml of the suspension taken by the formula: $833(c/V)\ (id_u)/\ (id_s)$.

  which V =volume in ml of the suspension taken

  id_u = diffusion current of the unknown solution

  id_s is that determined in a solution of USP Nitrofurantoin Reference Standard, the concentration of which C milligrams per mL

Data and Calculation

exactly 10 ml of Oral Suspension was taken for the assay. Polarogram of this dilution measured 12.45 cm. A polarogram of a reference standard solution containing 0.06 mg/ml measured 12 cm. Calculate the mg of Nitrofurantoin in the final dilution of Oral Suspension.

1) Determine the amount (mg) of Nitrofurantoin in the final dilution.

$$Cu = \frac{(Cs)\,(cm_u)}{cm_s} = \frac{0.06\ mg/ml \times 12.45}{12} = \mathbf{0.0622\ mg/ml}$$

2) Determine the volume in ml of the Oral Suspension in the final dilution.

10 : 100 = X : 3

X = 0.3 ml

0.3 : 25 = X : 1

X = 0.012 ml

3) The amount of Nitrofurantoin in 100 ml of Oral Suspension is:

$$0.0622 : 0.012 = X : 100$$

$$X = 518 \text{ mg}$$

PHARMACEUTICAL APPLICATIONS

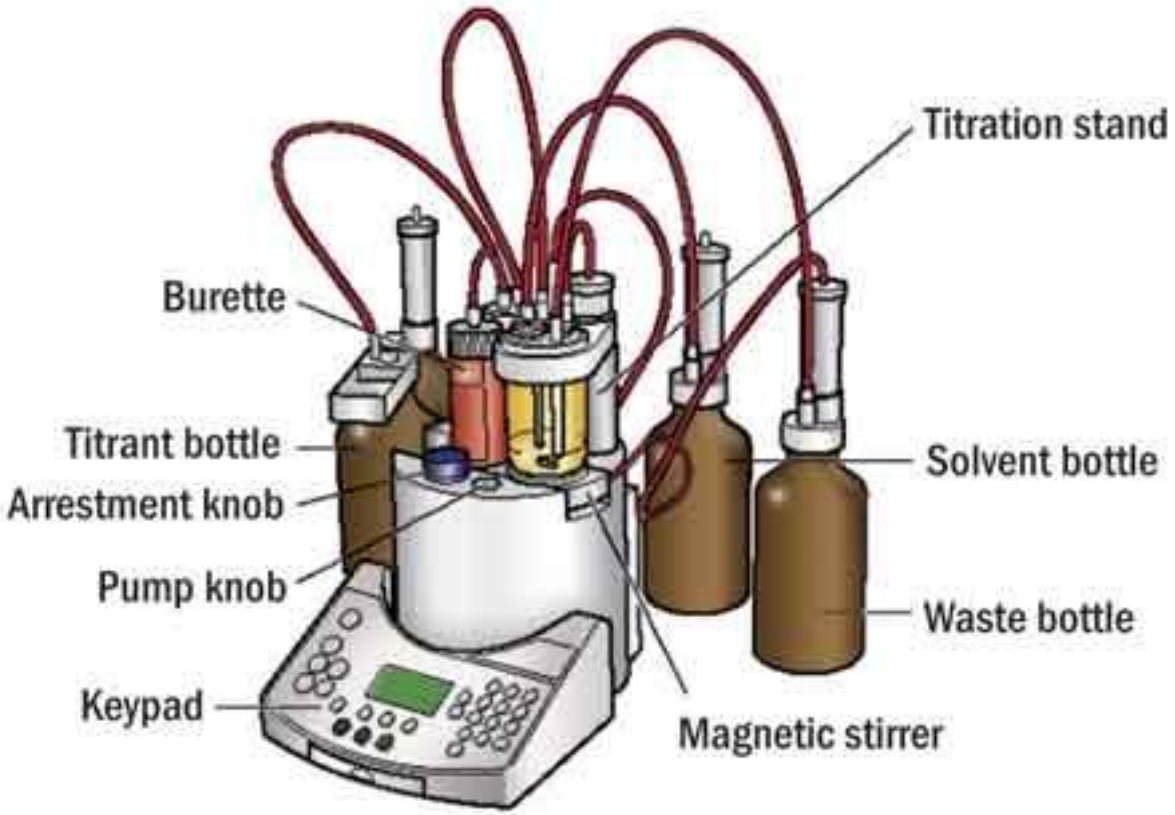
- Dissolved oxygen and peroxides
- Trace metals and metal –containing drugs
- Antiseptics and insecticides
- Vitamins
- Hormones
- Antibiotics
- Alkaloids
- Blood serum and cancer diagnosis

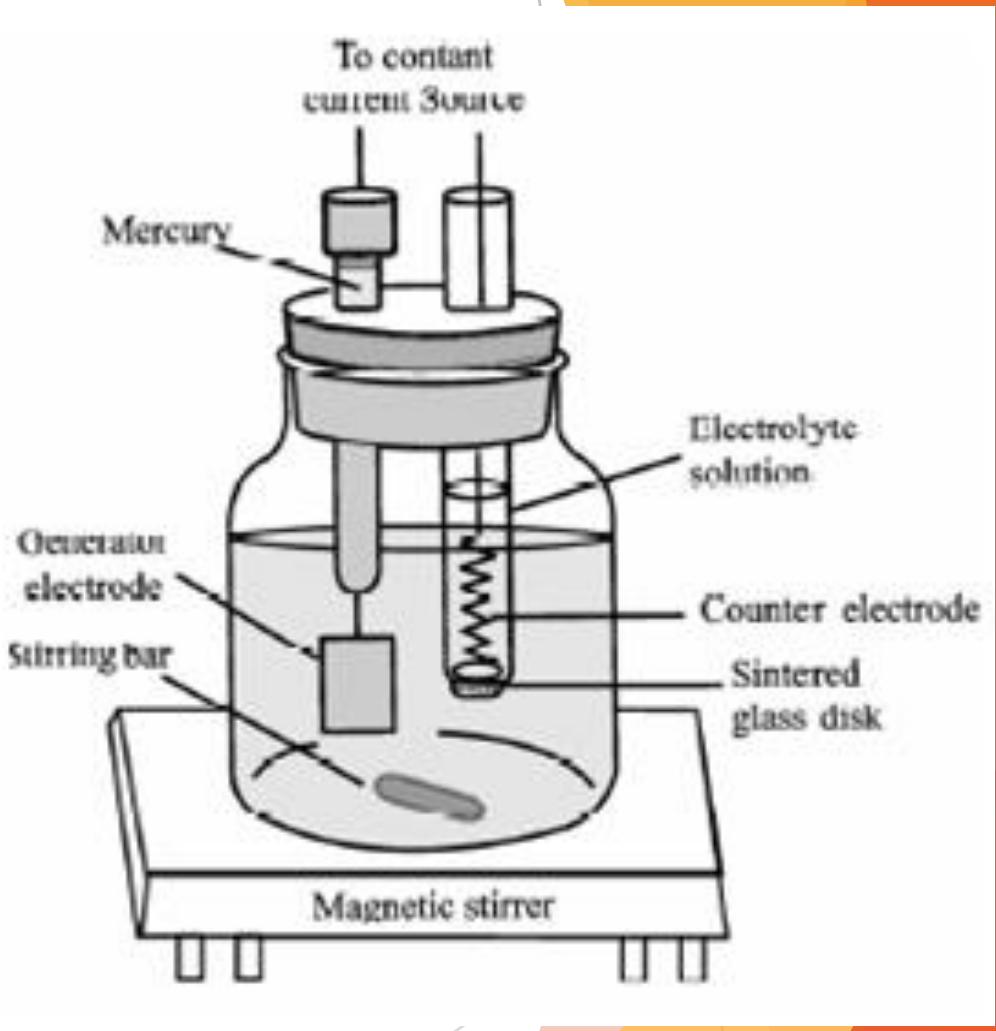
Coulometric Analysis

- Coulometric Analysis
  - Defined as an electroanalytical method in which the quantity consumed during an electrolysis reaction is a measure of the electroactive species being analyzed.
  - Objective:
    - To measure accurately the quantity of electricity consumed by the analyte species during the quantitative electrochemical reaction.

$$W = Q_f = \frac{M}{n}$$

W = weight of analyte
M = molecular weight
n= number of electrons involved in the electrochemical


Titration stand
Burette
Titrant bottle
Arrestment knob
Pump knob
Solvent bottle
Waste bottle
Keypad
Magnetic stirrer


To contant
Mercury
Electrolyte
solution
electrode
Counter electrode
Stirring bar
Sintered
glass disk
Magnetic stirrer

- **By Karl Fischer**

- It is used to determine the amount of water in a sample.
- It can determine concentrations of water on the order of milligrams per liter.
- It is used to find the amount of water in substances such as **butter**, **sugar**, **cheese**, **paper**, **and** **petroleum**.

Thank you