ELECTROANALYTICAL TECHNIQUES-5

Lecture 5

By

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Pop Quiz !!

- Normal Polarography has limitations at low conc because of

Interference due to residual current

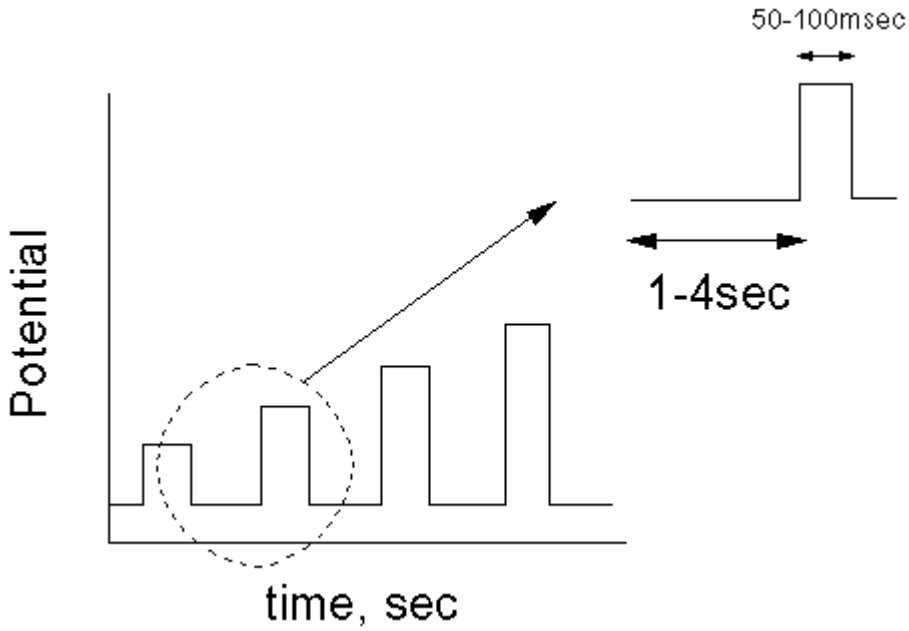
We cannot reduce ions at low conc

We cannot oxidise at low conc

I Don’t know sir, I was busy talking to my friend

Pop Quiz !!

- Which kind of pulse polarography is this

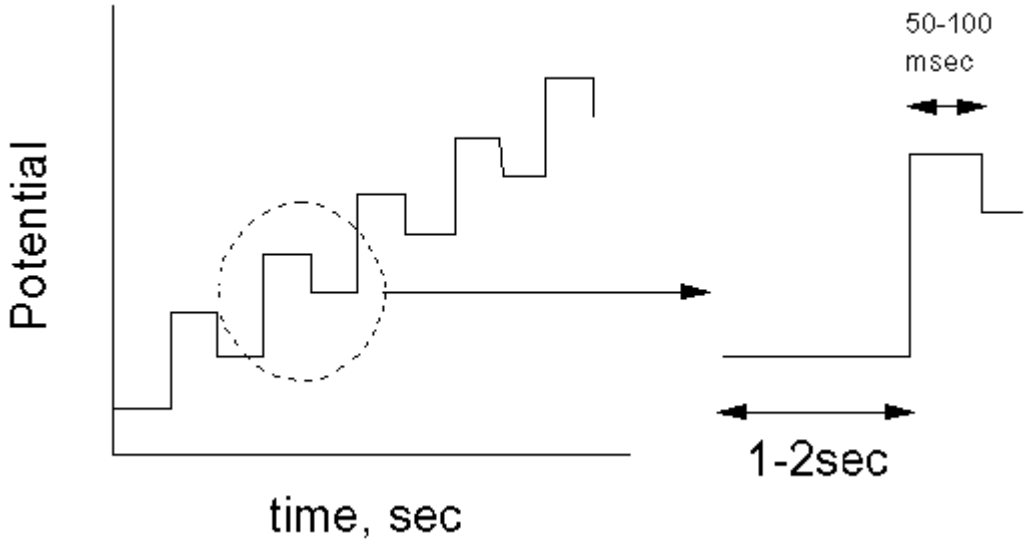


NORMAL

DIFFERENTIATED

Pop Quiz !!

- Which kind of pulse polarography is this



SQUARE WAVE

DIFFERENTIATED

Pop Quiz !!

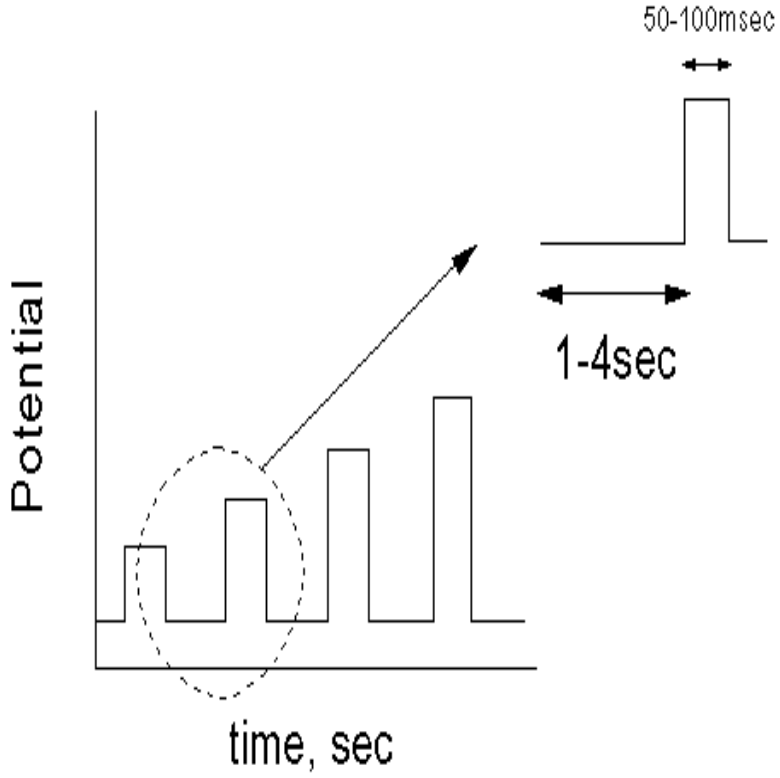
- I have a mixture of three metal ions, X, Y, Z. There Half-wave potentials are X=1.1 V, Y=1.15V, Z=1.1.0 V. Can I analyse/detect them using polarography?? Explain answer

NO

YES

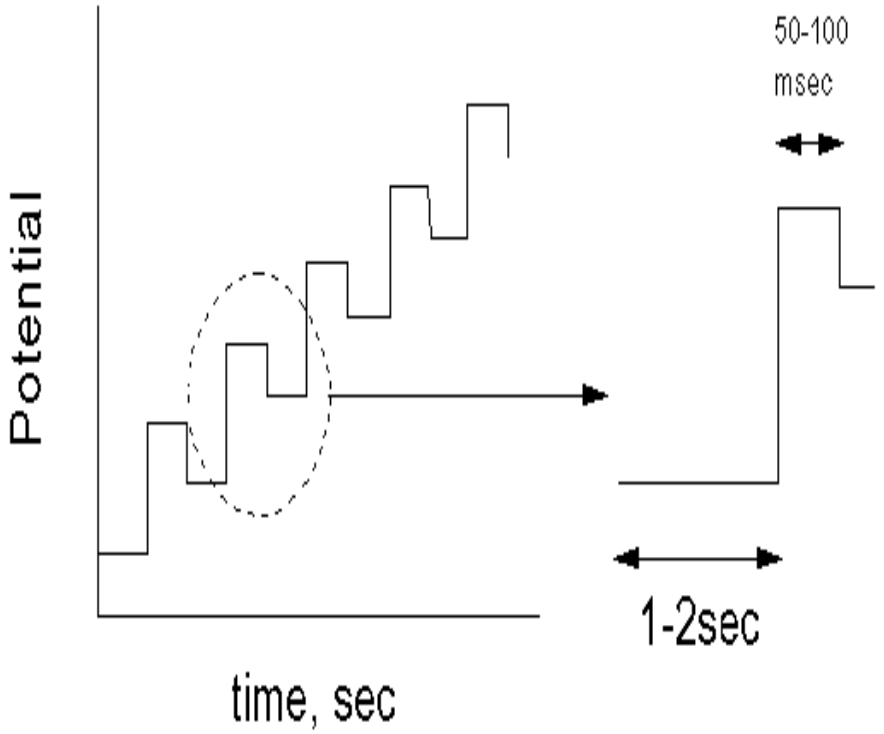
Normal Pulse Polarography

- Normal Pulse Polarography:
  - Each potential step begins at the same value (a potential at which no faradaic electrochemistry occurs)
  - Discrete potential steps at the end of the drop lifetime (usually during the last 50-100 ms of the drop life which is typically 2-4 s)
  - Amplitude of each subsequent step increases in small increments
  - After the initial potential step, the capacitive current decays exponentially
  - The diffusion current is measured just before the drop is falls, allowing excellent discrimination against the background capacitive current

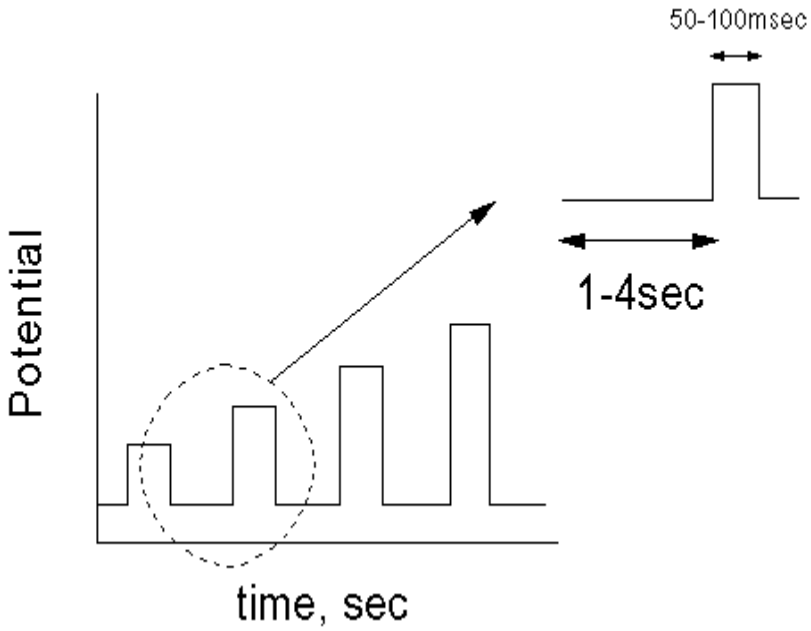


Differentiated Pulse Polarography

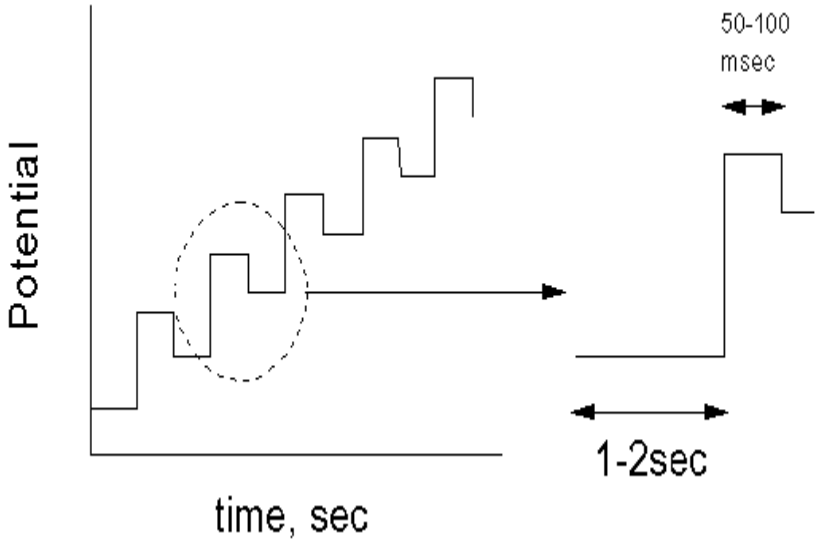
- Similar to normal pulse polarography however <u>difference is same amplitude of potential</u>
- Differentiated Pulse Polarography
  - Potential increased in form of **<u>pulses</u>**
  - Pulse height (5- 100 mV)
  - Current measured twice
    1. Before application of pulse
    2. End of pulse
- Better ability to discriminate against capacitive current because it measures a difference
- Current detection limit of 10^{-8} M



Normal vs Differentiated Pulse Polarography



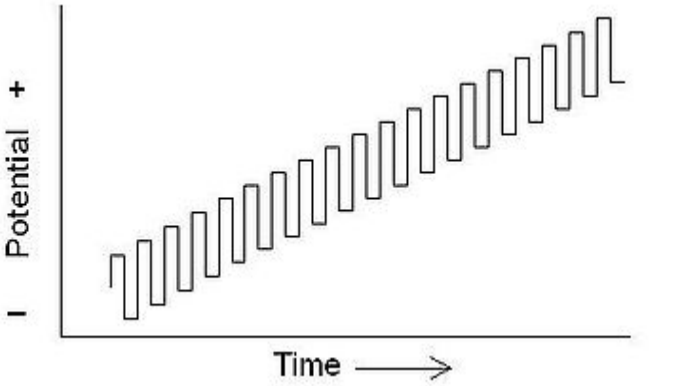
Normal Pulse Polarography

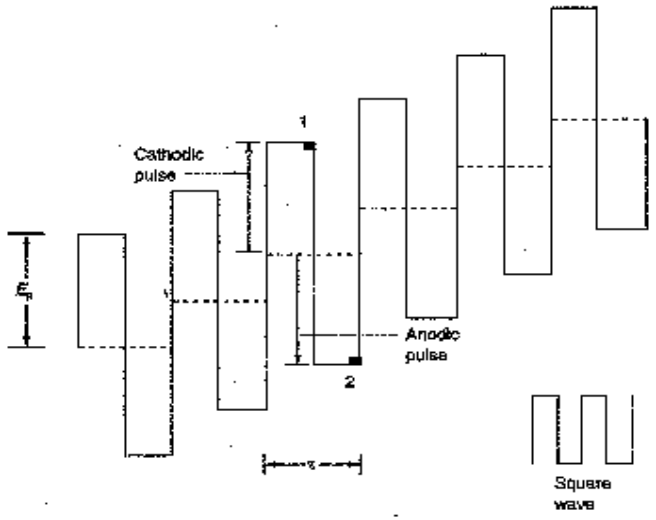


Differentiated Pulse Polarography

Square Wave Polarography

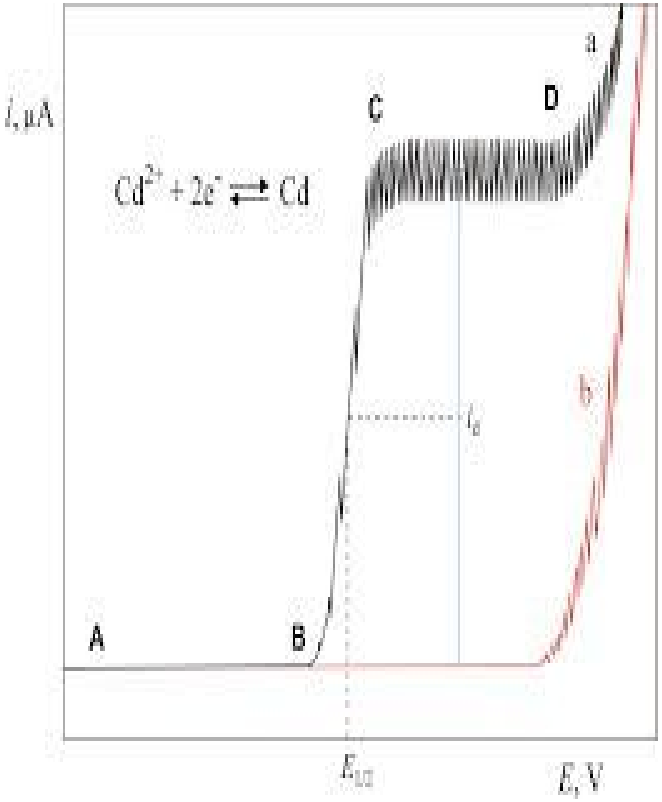
- Voltage applied in form of alternating wave (Positive, negative, positive…)
- Current sampled at start & end of pulse
- Alternating cathodic & anodic pulse
- Advantages
  - Very fast method (100 times, <1 S)
  - Very sensitive as well (nano molar levels)





Amperometric Titrations

- Limiting current independent of voltage
- Depends on rate of diffusion of electroactive material towards electrode
- Diffusion current proportional to conc of electroactive material
- Amperometric titration principle:
  - Add reagent that removes/adds electroactive material
  - Current increases/decreases due to loss/gain in electroactive material

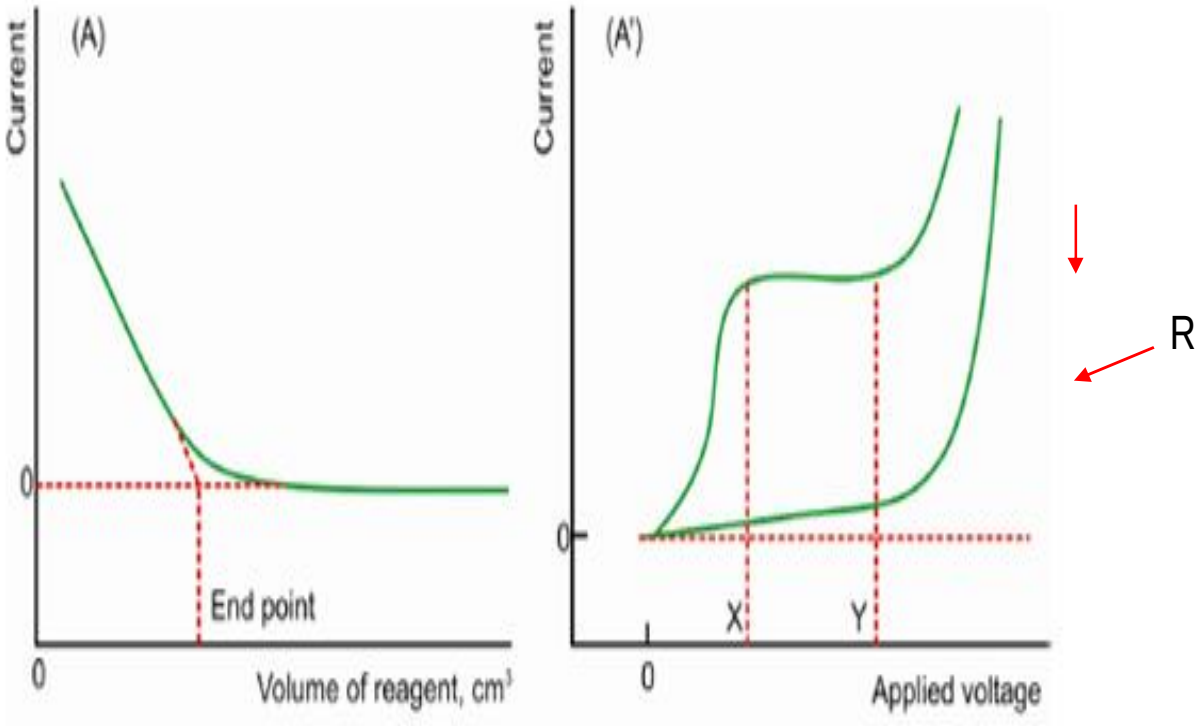


Amperometric Titrations

- Current-voltage polarograms in supporting electrolyte must be determined
- Voltage applied = total diffusion current of analyte, reagent or both
- Four common end points used, S= analyte, R = reagent

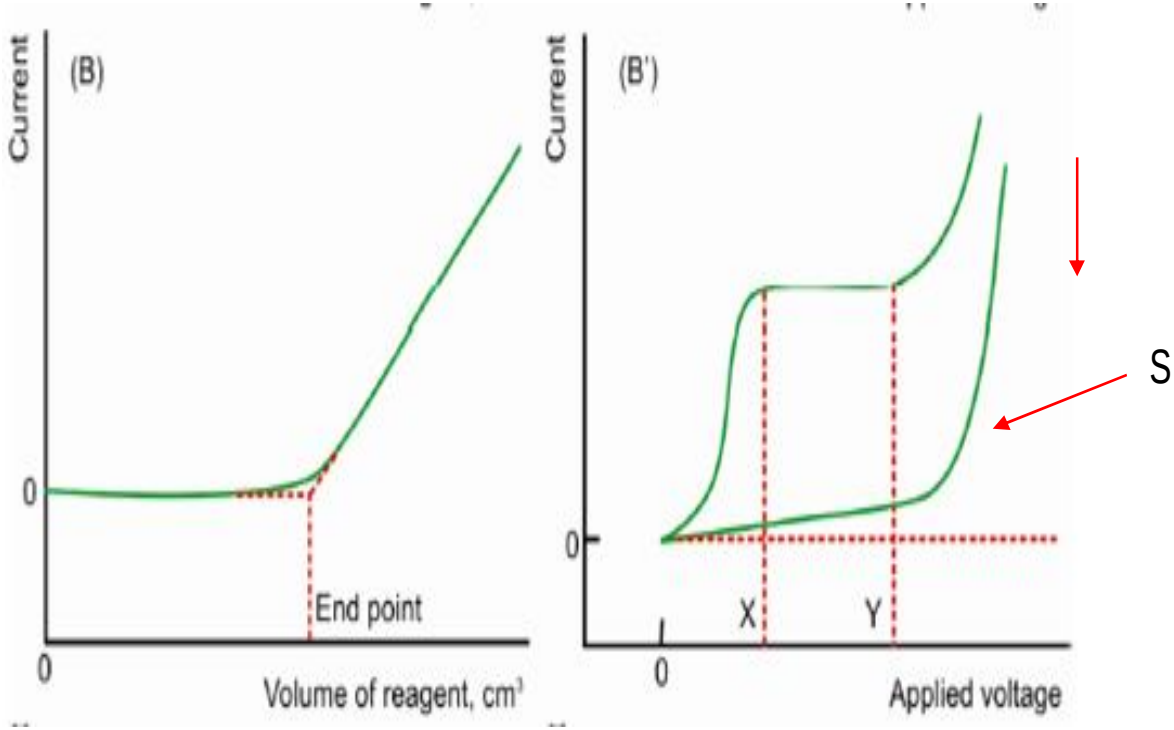
Amperometric Titrations (End Point Type 1)

- Only Analyte (S) gives current
- Addition of reagent (R) decreases current
- Between X – Y, R does not give any diffusion current
- S is removed by R (inactive) by precipitation
- Ex. Lead titrated by sulphate ions



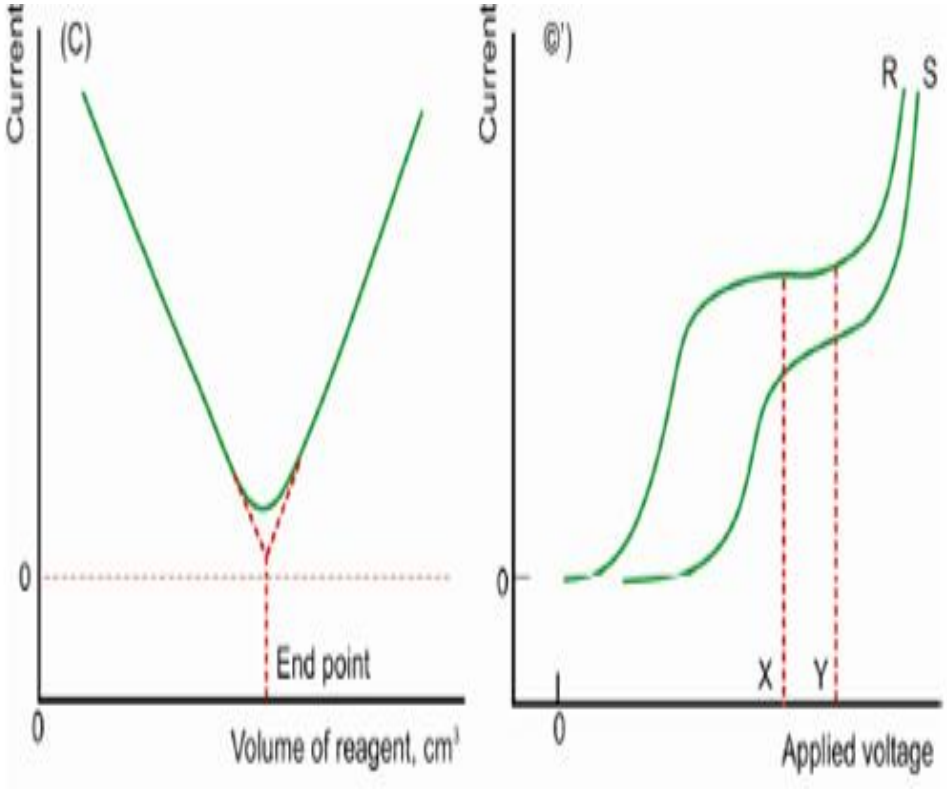
Amperometric Titrations (End Point Type 2)

- Reagent is active, give diffusion current
- Analyte (S) is inactive does not give any diffusion current
- Electroactive reagent + inactive substance (S)
- Ex. Sulphate ions titrated with Pb



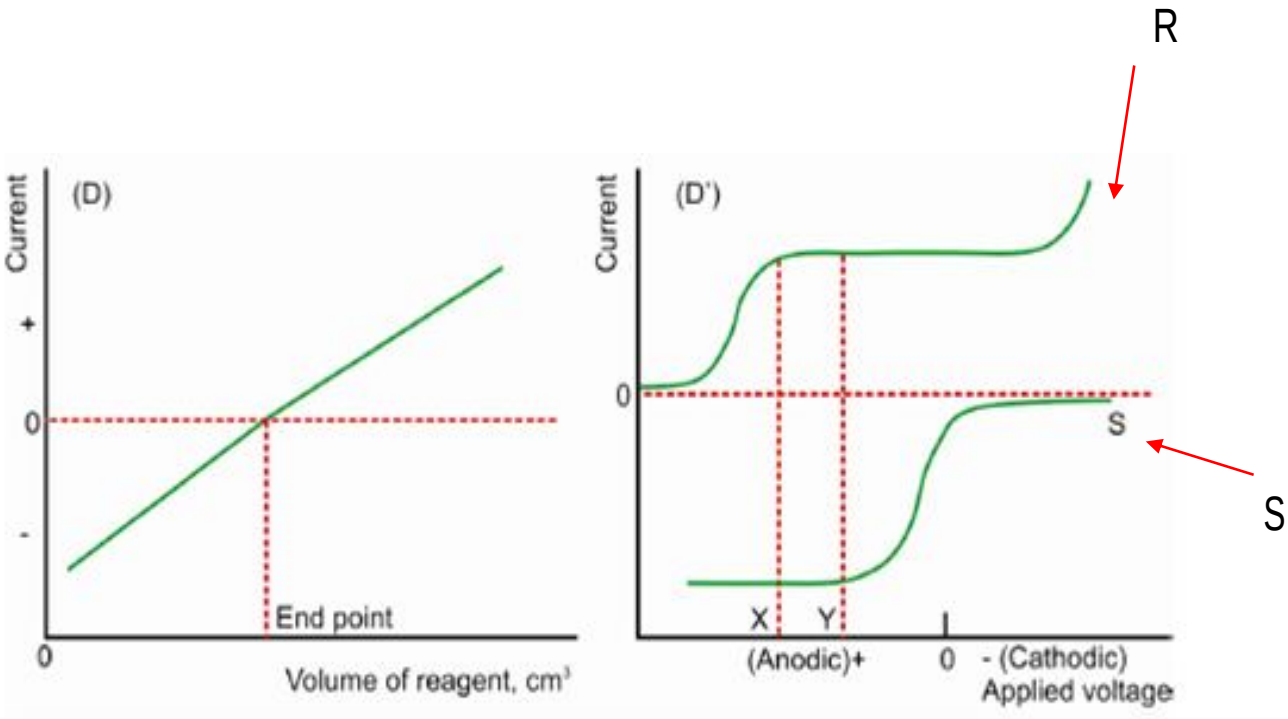
Amperometric Titrations (End Point 3)

- Both Reagent (R) and Analyte (S) give diffusion current
- V-shaped curve is obtained
- Ex. Pb with Chromate ions



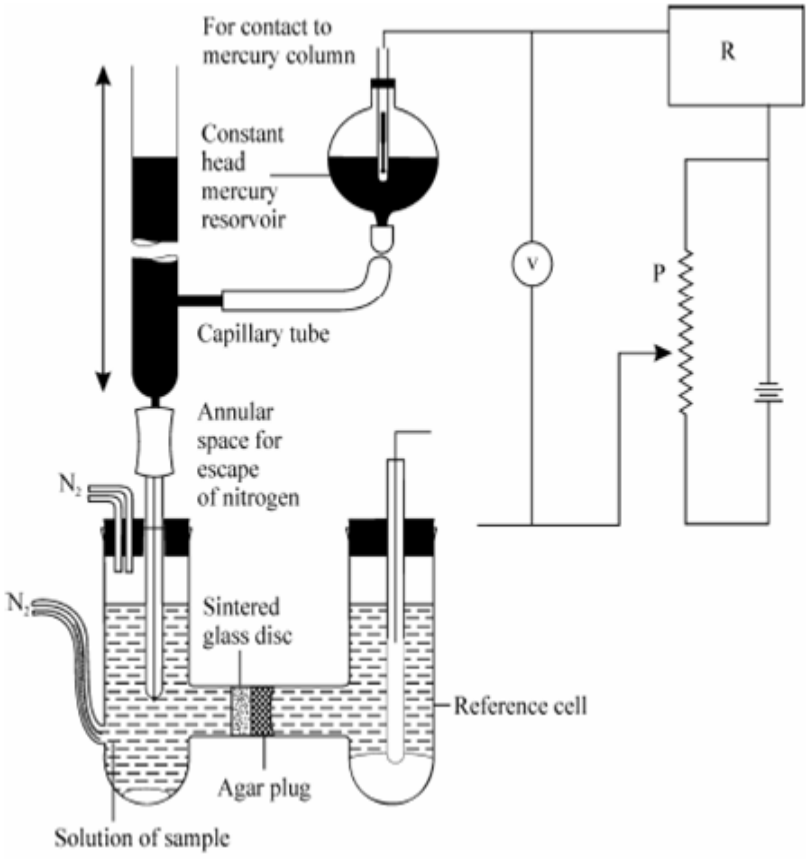
Amperometric Titrations (End Point 4)

- Solute (S) give anodic diffusion current
- Current changes from anodic to cathodic, vice versa
- End point indicated by zero current



Amperometric Titrations with DME

- Burette, DME, passage for nitrogen gas
- Applied voltage controlled by variable resistance
- Procedure:
  1. Known volume of analyte in beaker
  2. Dissolved oxygen removed
  3. Applied potential adjusted to desired value
  4. Known volume of reagent added
  5. Current , burette reading noted
  6. Enough readings to plot intersection point, end point



Biamperometric titrations

- Titrations also done with 2 small Pt electrodes- low emf applied (1-100 mV)
- End point – Appearance or disappearance of current
- Requirement: reversible redox system before or after end point

Biamperometric titrations: concept

- Titrations with 2 indicator electrodes, reactant involves reversible system ($I^2 + 2e = 2I^-$)
- Current flows through cell
- Oxidised form reduced at cathode = amount formed by oxidation of reduced form
- Both electrodes polarized until oxi or red form consumed by titrant
- After end point only one electrode remains polarized
- No current flows at or after end point

Biamperometric titrations Apparatus

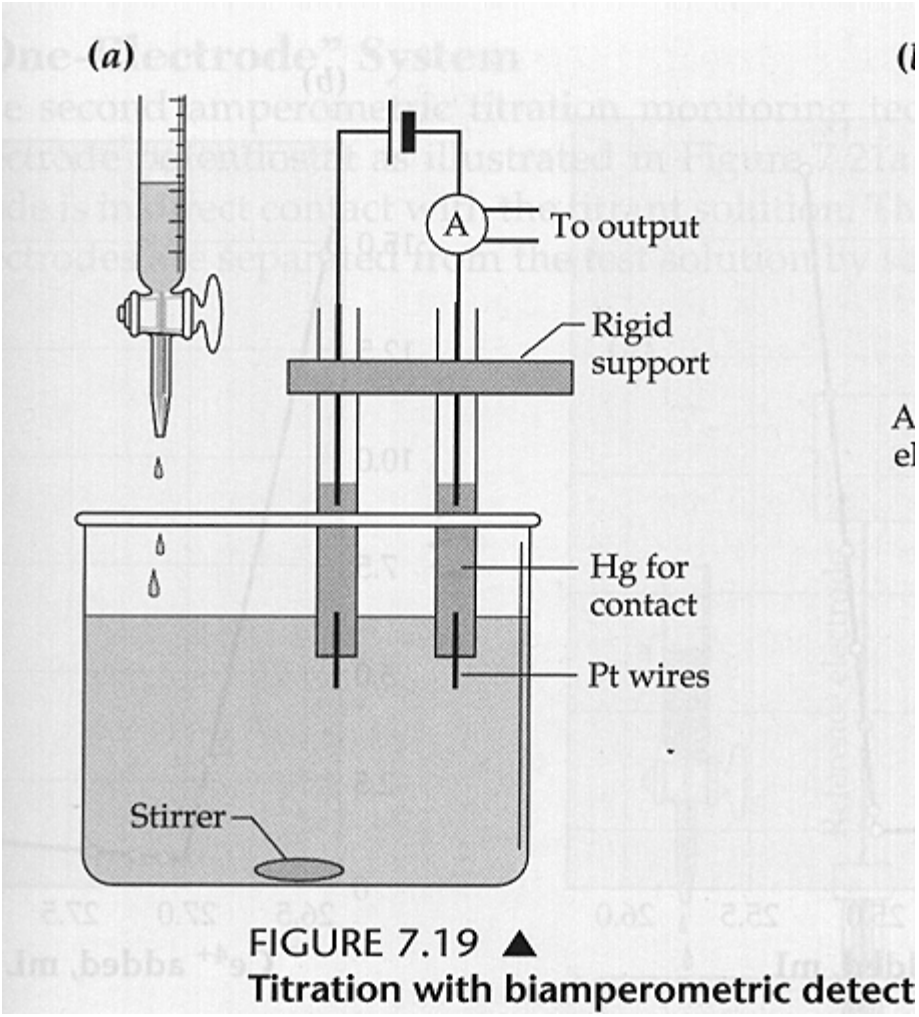


FIGURE 7.19 ▲
Titration with biamperometric detect

Advantages of Biamperometric titrations

- Rapid method (end point graphic, few measurements before/after)
- Capable where other methods fail (potentiometric, visual indicator)
  - Precipitations, hydrolysation doesn't matter since end point is obtained from several readings
- Lower limit of detection compared to other methods (10^{-4} M)
- Foreign salts if present in solution do not interfere (Some of them even added as supporting electrolyte)

Applications

- Complexation reactions:
  - Titration of metal ion + EDTA
  - Potential selected so that EDTA, EDTA+ion complex not reduced
  - So when EDTA added to ion, current decreases
  - Example: Zinc + EDTA alkaline medium at -1.4 V
  - Bismuth ions + EDTA at pH 1-2 at -0.2V
- Precipitation reactions:
  - Pb using potassium dichromate
  - Sulphate using lead nitrate