ELECTROANALYTICAL TECHNIQUES-4

Lecture 4

By

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What is Voltammetry ???

Analyte electrolytically deposited upon electrode & then weighed

Analyte determined by quantitative reaction during electrolysis

Analyte determined by measuring electrode potential of ions compared to reference

Analyte determined by measuring current that is related to conc of analyte by application of potential

Pop Quiz !!

- Polarography is a sub class of voltammetry where the working electrode is

Dropping iron

Dropping mercury

Dropping copper

I Don’t know sir, too busy with my periodic exam !!

Pop Quiz !!

- Major advantage of dropping mercury electrode is that it

It provides cool looking mercury

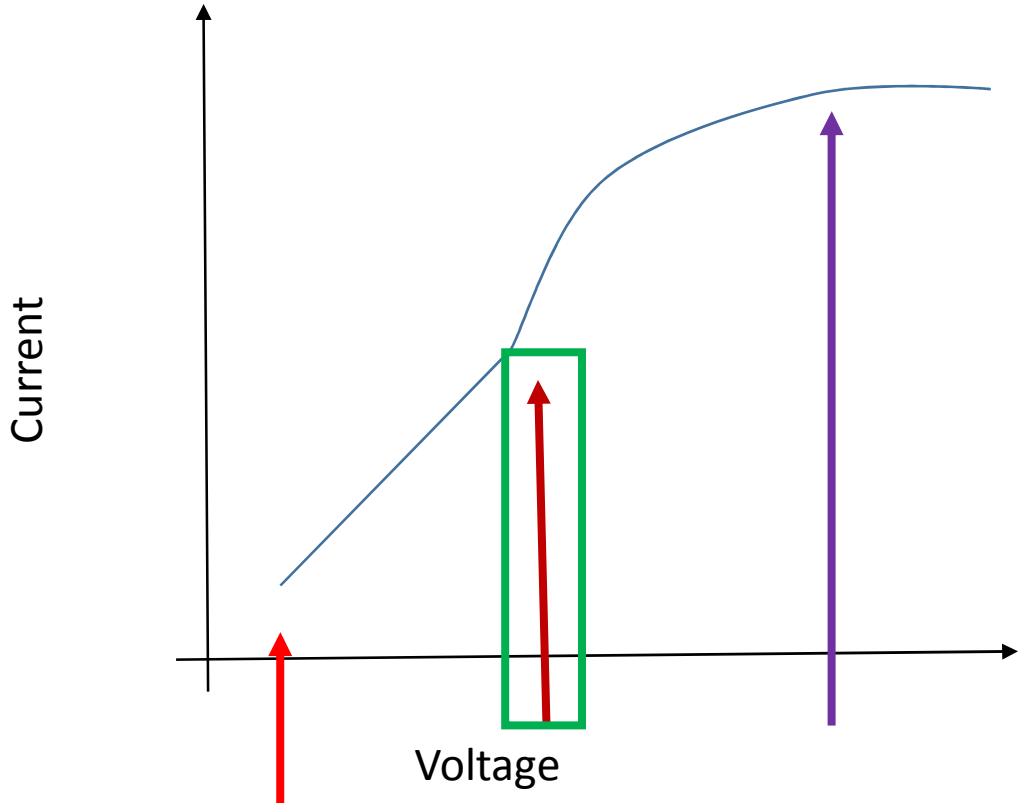
Mercury surface is easily reducible

Provides fresh, replaceable working electrode surface at each drop

Can I call “Mercury man” use of lifeline ??

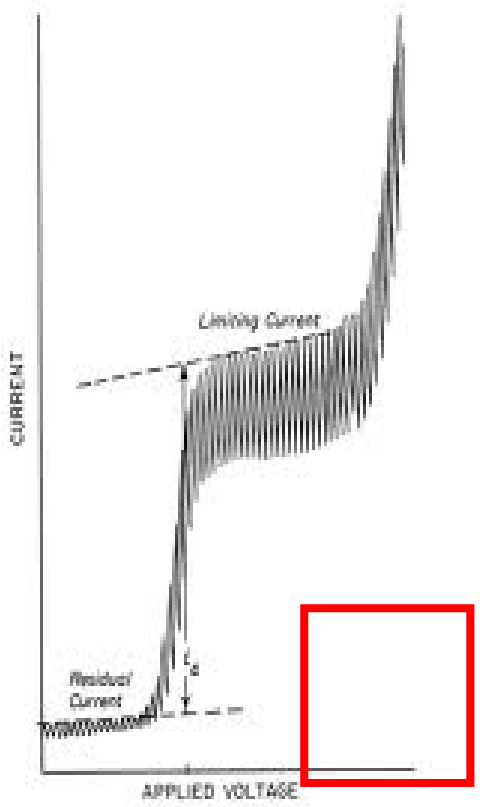
Pop Quiz !!

- Half-wave potential is



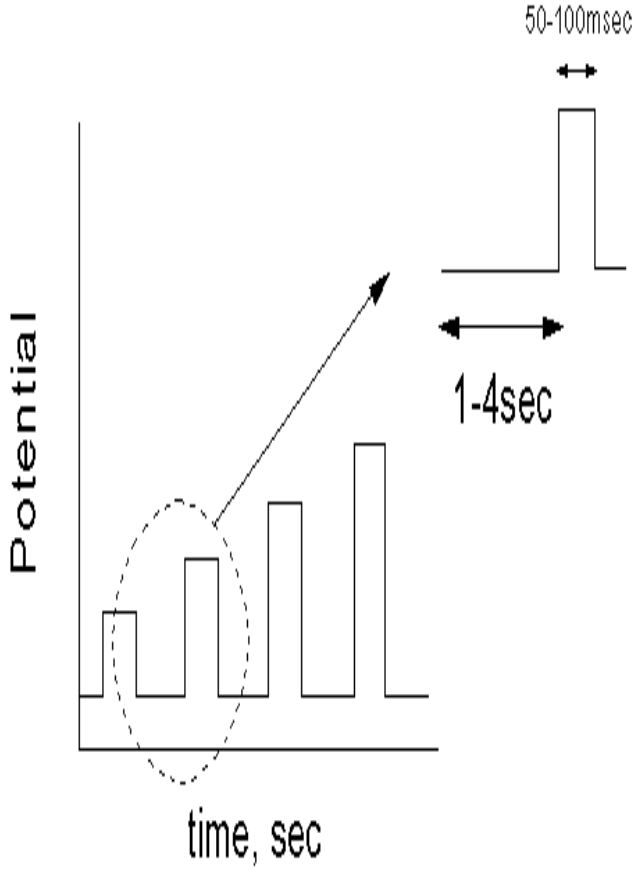
Limitations of Normal Polarography

- Normal polarography works best above 100 uM (moderate concentrations), this is a limitation
- Condenser current (capacitance, charging) leads to interference
- Barker & Jenkins overcame this problem by applying series of pulse during lifetime of mercury drop
- We will talk about several modifications to nature of pulse applied
    1. Normal
    2. Differentiated
    3. Square wave



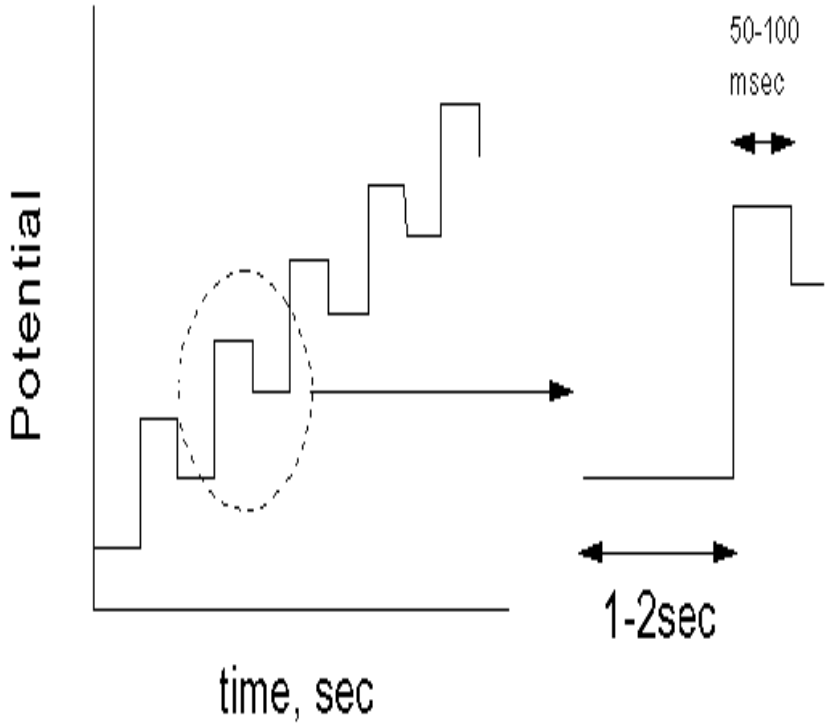
Normal Pulse Polarography

- 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

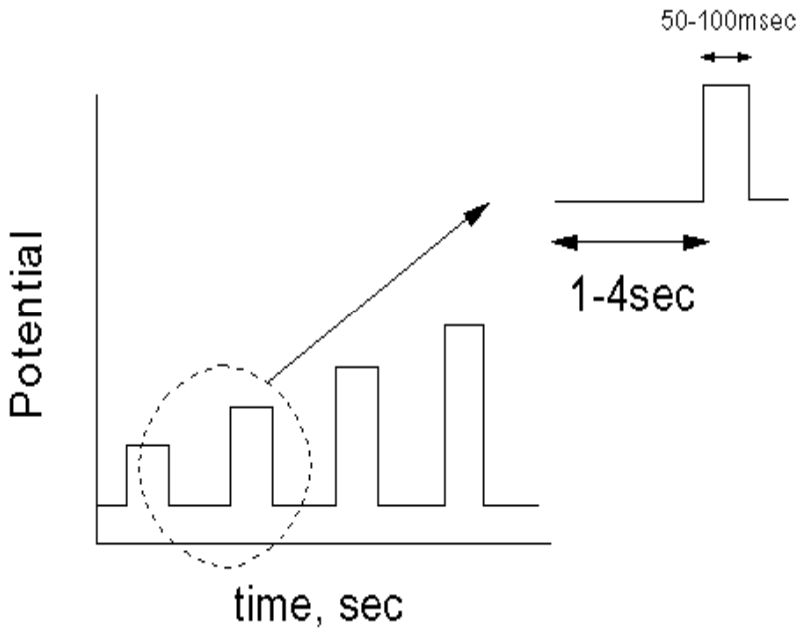


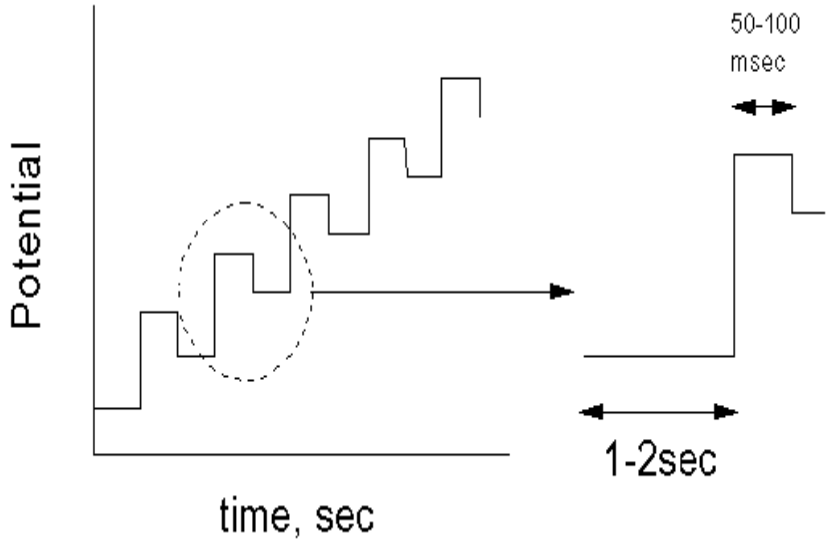
Differentiated Pulse Polarography

- Similar to normal pulse polarography however difference is same amplitude of potential
- Differentiated Pulse Polarography
  - Potential increased in form of **pulses**
  - 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



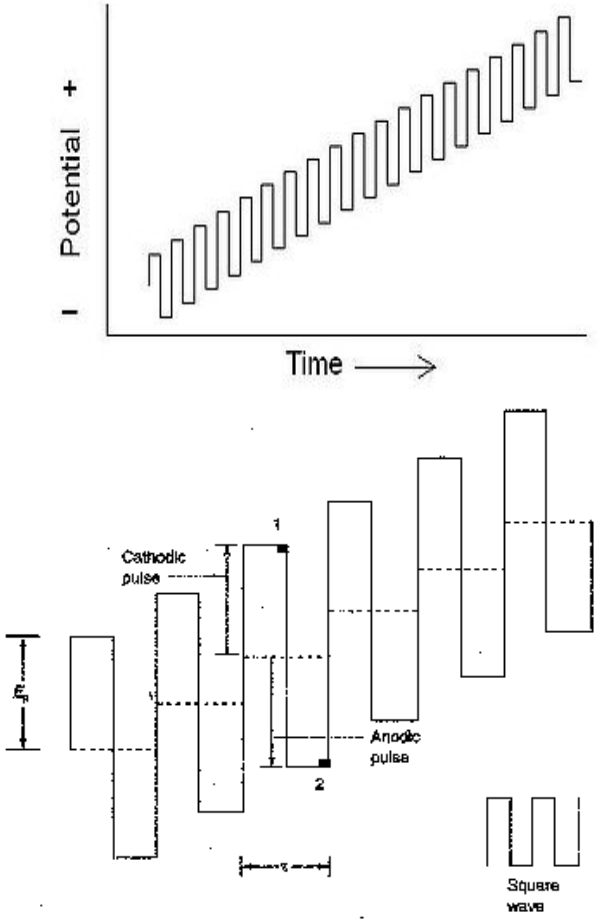


Normal Pulse Polarography

Differentiated Pulse Polarograph

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)



Applications of Polarography

- Detection of In-organic compounds
  - Estimation of cations & anions in presence of interfering ions
  - Mixture of ions determined if half –wave potential separated by at least 0.2 V
  - Series of reducible substances can be estimated in one solution
  - Typical cations: Cu, Bi, Pb, Cd, Zn
  - Typical areas of application: metals, plating solution, food & beverages, fertilizers, cosmetics, drugs, industrial effluents

Applications of Polarography

- Detection of organic compounds
  - Reactions more complex, interpretation more difficult
  - Involve both reversible & non-reversible reduction (most)
  - Reversible reductions mostly involve: quinone, phenyl amine
  - Generally involve hydrogen ions, reactions pH dependent
  - $R + nH^+ + ne = RH_n$
  - Half-wave potential is pH dependent

  - Example:
  - Benzaldehyde reduced in <u>alkaline sol</u> to benzyl alcohol
  - $C_6H_5CHO + 2H^+ + 2e = C_6H_5CH_2OH$ (wave at –1.4V, alkaline)

  - Benzaldehyde reduced in <u>acidic sol</u> to Hydrobenzoin in acidic
  - $2C_6H_5CHO + 2H^+ + 2e = C_6H_5CHOHC_6H_5$ (wave at –1.0V, acidic, pH<2)

Applications of Polarography

- Determining total & individual plant components
- Pharmaceuticals:
  - Epinephrine, norepinephrine
  - Local anesthetics
  - Tetracycline
  - Sulphonamides
- Determination of dissolved Oxygen