ELECTROANALYTICAL TECHNIQUES-7

Lecture 7

By

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Coulometry

- Analytical methods based on measurement of quantity of electricity
- Coulometric analysis is application of faraday's law
  - Extent of chemical reaction is directly proportional to current
- Fundamental requirement for coulometric analysis:
  - Electrode reaction proceeds with 100 % efficiency at working electrode
  - So that we can apply faraday's first law for analysis

Coulometry Titrations

- Coulometry Titrations can be done in TWO ways
  1. Fixed potential of working electrode (potentiostatic)
  2. Fixed current (Amperostatic)

1. Potentiostatic:
   - Substance reacts at working electrode with 100 % efficiency
   - Completion of reaction indicated by current reducing to zero
2. Amperostatic:
   - Solution of substance to be determined is electrolyzed with constant current until reaction is complete
   - Total quantity of electricity = current X time

Amperostatic Coulometry

- Limitations of coulometry at constant potential
- At constant current, large number of substances can be determined
- This includes many substances that do not react quantitatively at electrode

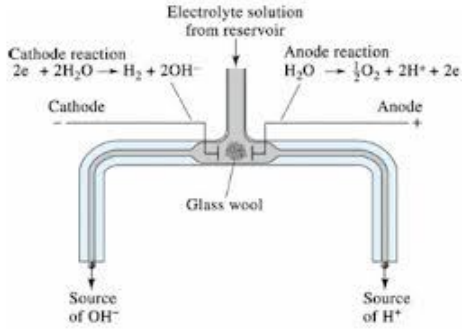
Types of Coulometry titrations

- Primary Coulometric Titration:
  - Substance to be determined oxidized/reduced at one of the electrode
  - Substance reacts directly at electrode
  - No other substance should be electrolysable
  - Electron becomes standard reagent

- Secondary Coulometric Titration:
  - Active intermediate first produced quantitatively by electrode process
  - This intermediate then reacts directly with substance to be determined
  - Quantity of substance reacted can be calculated by faraday's law
  - Fundamental Requirement:
    1. Reagent generating reaction proceeds with 100 % efficiency
    2. Generated reagent reacts rapidly/stoichiometrically with substance

External generation of titrant

- Reagent generated externally , delivered to titration cell
- Reagent generated electrolytically
- Double arm electrolytic cell
- Generator electrode consists of two pt spirals
- As the solution of electrolyte flows, electrolysis occurs at electrode
- Product of electrolysis are swept underflow to cells
- Minor disadvantage:
  - Dilution of titration vessel



External Generator Cell

Advantages of Coulometric Titrations

- Highly sensitive method, both time/current can be measured with high accuracy
- Unstable reagents can be used (Br, Cl, Silver(II) ion, generated, consumed immediately)
- Control over how much titrant is needed, good for micro, semi-micro scale work
- Sample solution is not diluted
- Titrant generating solution pretreated, this removes any impurities
- Method can be automated/remotely controlled, important for dangerous, radioactive substances

Applications of Coulometric Titrations

- Coulometric titrations developed for all type of titration reactions

- Neutralization reactions:

  - $2H_2O = O_2 + 4H^+ + 4e^-$ (Anode)
  - $2H_2O + 2e^- = H_2 + 2OH^-$ (Cathode)

  - Limiting reactions in aqueous solution, can be used to titrate Acid/Base
  - End point by pH meter

Applications of Coulometric Titrations

- Coulometric titrations developed for all type of titration reactions

- Complexation reactions:

  - Metal ions titrated by EDTA generated by electrode process
  - Hg-EDTA reagent is prepared by Hg-Amine-EDTA complex
  - EDTA releases from Hg-EDTA by electrolysis
  - EDTA complexes with metal ion of interest
  - End point detected potentiometrically
  - Ions detected: Zn, Pb, Cu, Ca

Applications of Coulometric Titrations

- Coulometric titrations developed for all type of titration reactions

- Precipitation reactions:
  - Use of mercuric ions (Hg) to titrate with halide ions (precipitation reaction)
  - Mercury ions can be generated with 100 % efficiency from mercury coated gold, mercury anodes
  - Detection/quantification of Cl, Br, I

  - Use of Ag(I) ions
  - Can be generated with 100 % efficiency at silver anode

Applications of Coulometric Titrations

- Coulometric titrations developed for <u>all type of titration reactions</u>

- <u>Oxidation-Reduction reactions:</u>
  - Numerous reagents generated coulometrically that can be used in Ox-Red reaction titrations
  - Most important is electrogenerated Br, I

  - $2Br^- = Br_2 + 2e^-$ Bromine generated by oxidation of bromide ion)
  - Versatile, can be used in determination of various organic compounds (phenols, aromatic amines ..)