

Amperometric Titrations

Introduction to Amperometric Titrations

Definition:

- In amperometric titrations, a constant potential is applied to the working electrode, and the resulting current is measured as the titrant is added.
- The change in current is used to detect the end point of the titration.

Principle:

- The applied potential is chosen such that either the analyte or the titrant is electroactive (i.e., undergoes oxidation or reduction).
- As titrant is added, the concentration of the electroactive species changes, leading to change in current.
- A plot of **current vs. volume of titrant** shows a distinct **break point** (end point).
- The method is called amperometric because current is measured (amperes) instead of voltage.

Instrumentation:

1. Working Electrode:

- Often platinum, mercury, or glassy carbon.

2. Reference Electrode:

- Usually calomel or Ag/AgCl.

3. Electrochemical Cell:

- Contains the analyte and supporting electrolyte.

4. Potentiostat:

- Maintains constant applied potential.

5. Microammeter or Galvanostat:

- Measures the current.

Types of Amperometric Titrations:

- **Titration of reducible species** (e.g., using oxidants like KMnO_4)
- **Titration of oxidizable species** (e.g., using reducing agents)
- **Precipitation titrations** (e.g., Ag^+ vs Cl^-)

Graphical Representation:

- A **current vs. titrant volume** plot is drawn.

- The **end point** is determined by the **intersection** of two linear segments.

Advantages:

- Sensitive and accurate
- Can be used for colored or turbid solutions
- Does not require an indicator

Limitations:

- Requires stable applied potential
- Only applicable when at least one species is electroactive
- Can be affected by adsorption on the electrode surface

Types of Electrodes Used in Amperometric Titrations

- In Amperometric titrations, **two types of electrodes** are involved:
 - Working Electrode (also called Indicator Electrode)
 - Reference Electrode

A. Working (Indicator) Electrode

This is the electrode at which the redox reaction takes place. The current is measured at this electrode.

Common Working Electrodes:

1. Dropping Mercury Electrode (DME):

- Common in classical amperometry.
- Produces a fresh, reproducible surface for each drop.
- Ideal for measuring reduction reactions (e.g., O₂, metal ions).
- Advantage: Minimizes contamination; has a well-defined diffusion layer.

2. Rotating Platinum Electrode:

- Used in modern instruments.
- Offers controlled hydrodynamics (rotation improves diffusion).
- Suitable for both oxidation and reduction reactions.

3. Glassy Carbon Electrode:

- Inert, chemically resistant, and can be polished.
- Useful for a wide range of redox systems.
- Can be used at both positive and negative potentials.

4. Gold and Silver Electrodes:

- Occasionally used for specific reactions involving halides or sulfur-containing compounds.
- Provide different overpotentials and catalytic properties.

B. Reference Electrode

A reference electrode provides a stable and known potential against which the working electrode's potential is measured. It does not participate in the redox reaction.

Common Reference Electrodes:

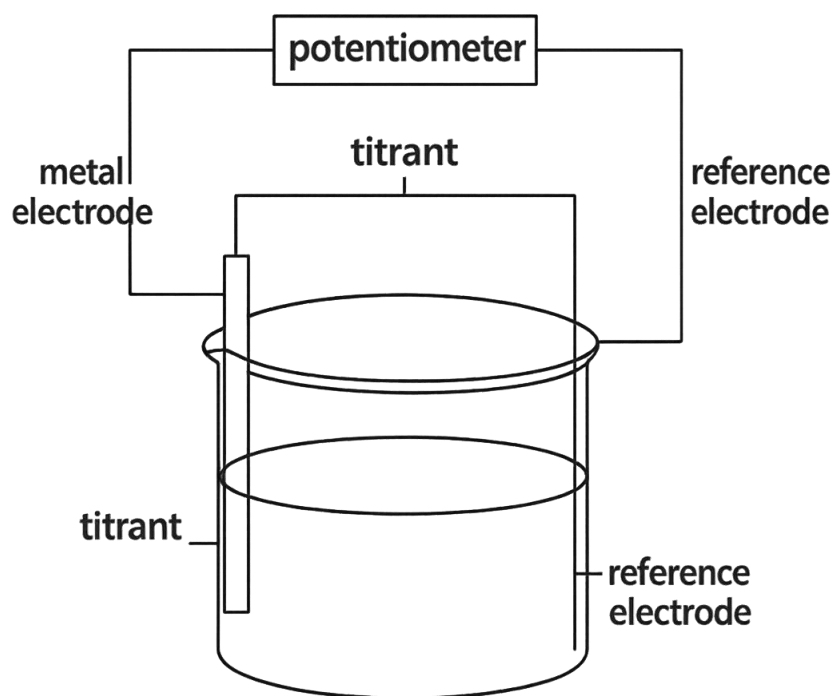
1. Saturated Calomel Electrode (SCE):

- Consists of mercury in contact with mercury(I) chloride and saturated KCl.
- Potential is stable and reproducible.

2. Silver/Silver Chloride Electrode (Ag/AgCl):

- Silver wire coated with AgCl and immersed in KCl.
- More environmentally friendly than SCE.
- Potential is also stable and commonly used in modern systems.

Instrumentation in Amperometric Titrations



- Amperometric titration setups are designed to **measure current at a fixed voltage** as a function of the amount of titrant added.
- The instrumentation is built to ensure accurate control and detection of electrochemical responses.

Basic Components of Amperometric Titration Setup:

A. Electrochemical Cell

- **Three-electrode or Two-electrode setup:**
 - A two-electrode system includes a working electrode and a reference electrode (which also may act as the counter electrode).
 - In high-precision setups, a three-electrode system is used:
 - **Working Electrode (Indicator)** – where the redox reaction occurs.
 - **Reference Electrode** – provides a constant reference potential.
 - **Auxiliary (Counter) Electrode** – completes the circuit and allows current flow.
- The electrochemical cell contains:
 - **Analyte solution**
 - **Supporting electrolyte** (e.g., KCl) to increase conductivity and minimize solution resistance.
 - **Stirring mechanism** to maintain homogeneous distribution of the titrant and enhance mass transfer.

B. Potentiostat / Galvanostat

- A **potentiostat** is the central instrument used in amperometry. It:
 - Maintains a constant potential between the working and reference electrodes.
 - Measures the current flowing between the working and counter electrodes.
 - Provides **electronic control**, ensuring high precision and sensitivity.
- A **galvanostat** maintains a constant current (less common in titrations), but modern systems can switch between modes.

C. Titrant Delivery System

- A burette or automated titration unit delivers titrant in small, controlled volumes.
- For high accuracy, computer-controlled syringe pumps are used to allow micro- or nano-liter additions.

D. Stirring Apparatus

- Typically a magnetic stirrer with a coated stir bar is used.
- Ensures uniform mixing and minimizes concentration gradients.

E. Data Acquisition System

- Interfaces with the potentiostat.
- Records and plots current vs. titrant volume or time.

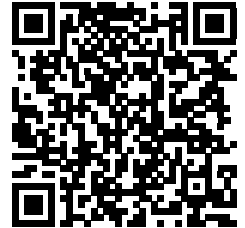


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