Electrochemical Cell

- **Electrochemical cell** is a system in which **chemical energy is converted into electrical energy** (or vice versa) through **oxidation–reduction (redox) reactions** occurring at spatially separated electrodes connected by an external circuit.
- System converting **chemical energy ↔ electrical energy** via redox reactions
  - Oxidation at anode.
  - Reduction at cathode.
  - Electron flow through external circuit by metal wire.
  - Ion flow through electrolytic solution or salt bridge.

Cathodes and Anodes

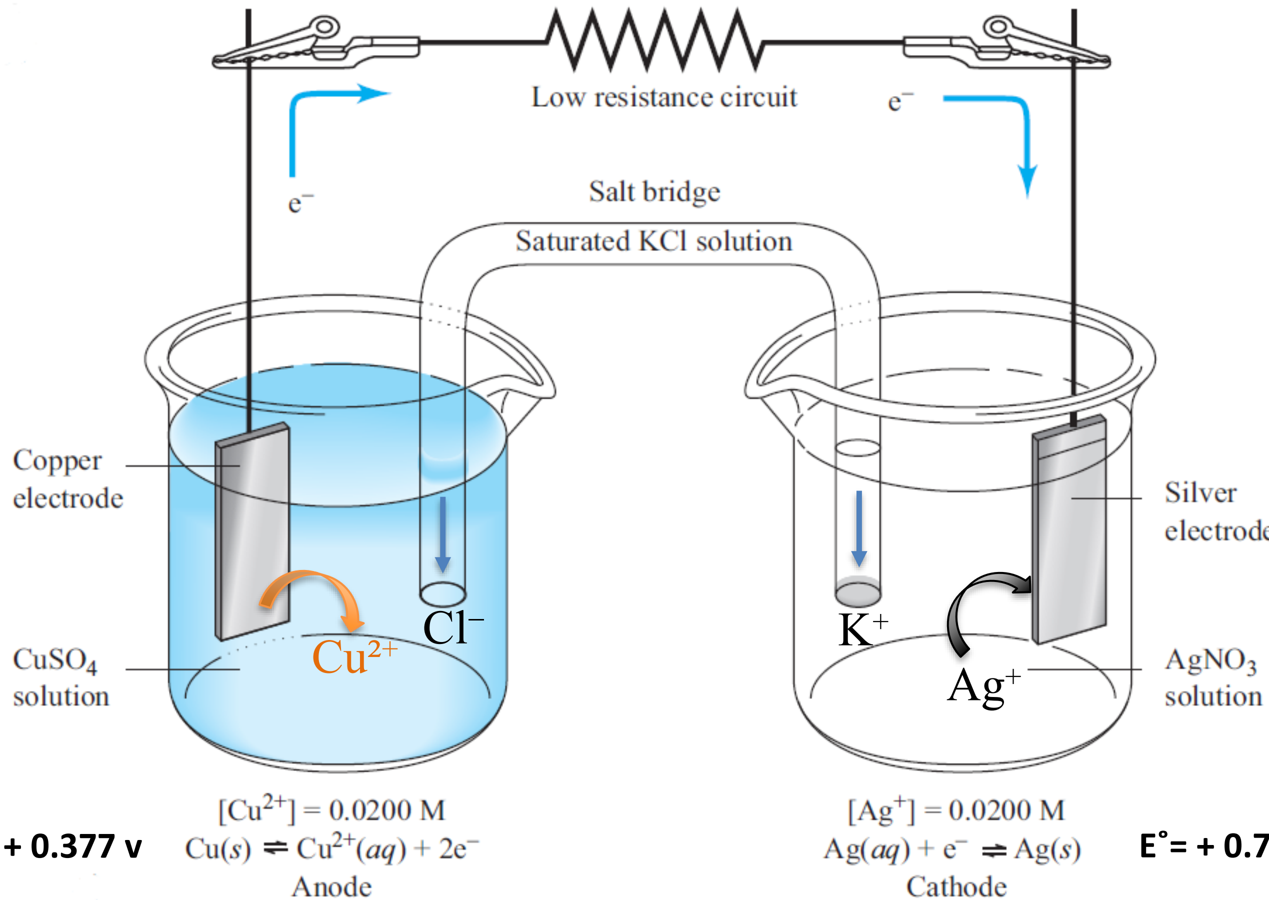
- A **cathode** in an electrochemical cell is the electrode at which reduction occurs.
- An **anode** is the electrode at which an oxidation takes place.
- **Electrons flow** from **anode → cathode**
- A **reducing agent** is an electron donor (loses electrons), Oxidation take place.
- An **oxidizing agent** is an electron acceptor (gains electrons), Reduction occur.

Type of electrochemical cells

1. **Galvanic cell (voltaic cell)**
2. **Electrolytic cell**
3. **Concentration cell**
4. **Full cell**

Type	**Purpose**	**Energy Conversion**
Galvanic (Voltaic)	Power generation	Chemical → Electrical
Electrolytic	Drive non-spontaneous reactions	Electrical → Chemical
Concentration cell	Measure activity differences	Chemical → Electrical
Fuel cell	Continuous energy production	Chemical → Electrical

1- Galvanic Cell (voltaic cell)



E° = + 0.377 v

E° = + 0.799 v

$$2Ag^{+}{}_{(l)} + Cu_{(s)} \leftrightharpoons 2Ag_{(s)} + Cu^{2+}{}_{(l)}$$

Essential components of a galvanic cell

1) Charge on Electrodes

- Electrodes can be metal (Zn, Cu) or inert (Pt, Au & C)
- Anode (**oxidation**); negative charge (**electrons generation by Cu oxidation**),
- Cathode (**reduction**); positive charge (**Ag^+ becomes part of electrode**)

2) Electrolyte

- Ionic conductor (aqueous solution have ions, molten salt, polymer)
- Movement of ions carrying electrical charge, so conduct electricity.

3) Salt Bridge / Ion-exchange membrane

- U shape glass tube salt bridges (consists saturated salt as such sat. KCl or sat. KNO_3) or Ionic liquid salt bridges or Filter paper bridges
- Completes the circuit or Maintains electroneutrality, Prevents solution mixing
- **Anions** migrate towards the **anode**, while **Cations** migrate towards the **cathode**

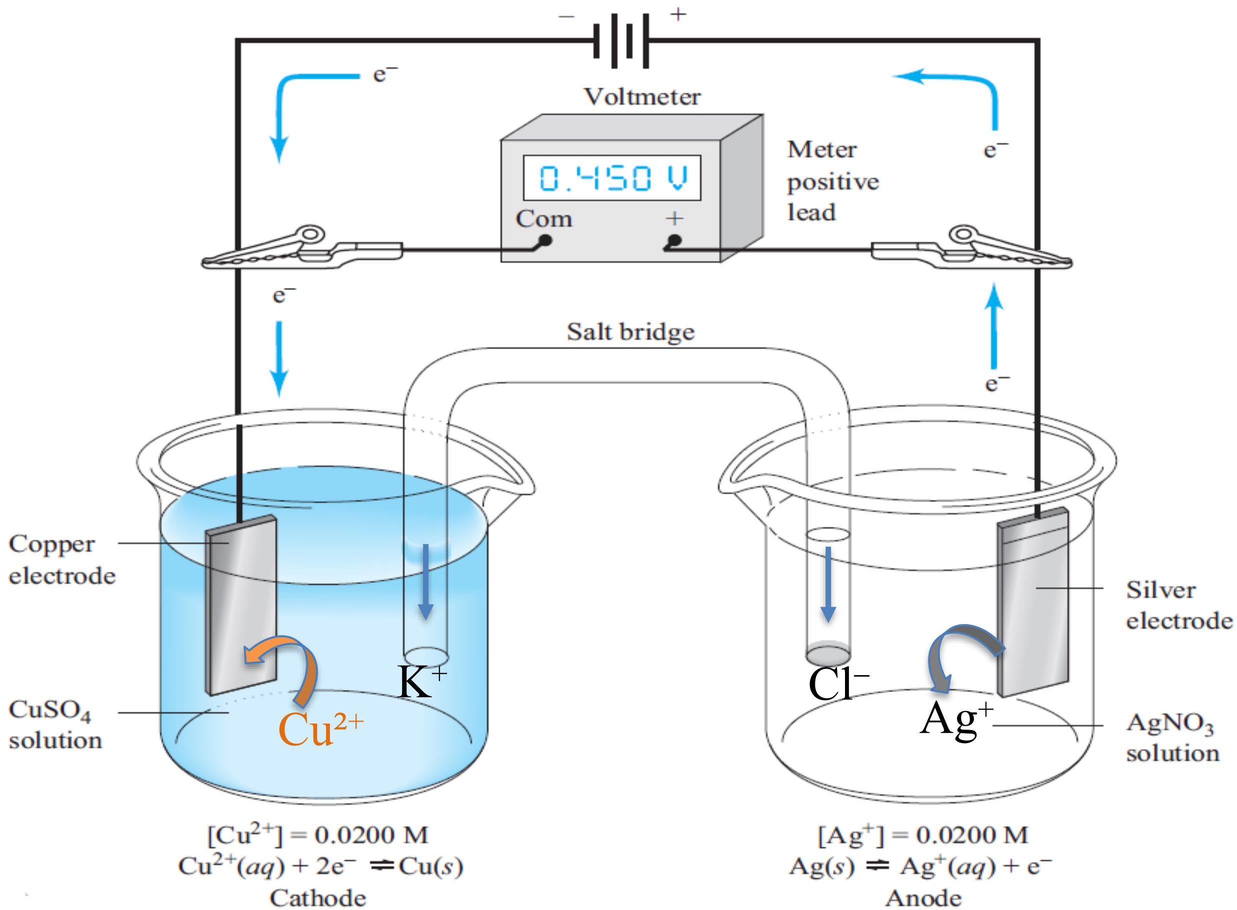
4) Conduction of charge

- Cu^{2+}enters anode solution (+ charge builds up); anions from salt bridge counter this +. Ag^+ leaves cathode solution (– charge builds up); cations from salt bridge counter this -.
- salt bridge maintains electrical neutrality (otherwise the reaction will quickly stop)

5) External Circuit

- Conducting wire or Load (resistor, device)
- **Electrons released** at the **anode** travel through external wire → load (**resistor, device**) → **cathode.**

2. Electrolytic Cell



$$2Ag_{(s)} + Cu^{2+}{}_{(l)} \leftrightharpoons 2Ag^{+}{}_{(l)} + Cu_{(s)}$$

1) An **electrolytic cell** requires an external power source such as (power supply or Battery), and a **galvanic cell** can be converted to operate as **electrolytic cell** by applying a voltage greater than its cell potential.

2) Charge on Electrodes:

- **The + positive terminal** of the power supply is connected to Ag (**anode**) and the **- negative terminal** to Cu (**cathode**).
- **Electrons** flow from the **- negative terminal** of power supply to the **Cu electrode**, causing **reduction** (**Cu^{2+} → Cu**) at the **cathode**. (**Cu^{2+} becomes part of electrode**).
- **Oxidation** (**Ag → Ag^{+}**) occurs at the **Ag electrode** (**electrons generation by Ag oxidation**), **supplying electrons** to the **+ positive terminal** of the power source.

3) In the electrolyte/salt bridge,:

- **anions** migrate to the **anode** and **cations** migrate to the **cathode** to maintain electroneutrality.
- Charge balance is maintained as **Ag^{+} accumulation** at the **anode solution** (+ charge builds up) is neutralized by **anions from salt bridge**, and **Cu^{2+} depletion** at the **cathode solution** (– charge builds up) is compensated by **cations from salt bridge**.

4) **External Circuit :**

- The **current direction** in an **electrolytic cell** is **opposite** to that in a **galvanic cell**, and **electrode roles are reversed**.
- The overall electrolytic reaction is **non-spontaneous** and is the reverse of the galvanic cell reaction.
- **Electrons** travel from **the rich electrons (- negative terminal** of power supply) through external wire → **cathode reduction of Cu occur** → the current is sustained by the **Anode oxidation of Ag occurs** → **(+ positive terminal** of power supply).

- **Galvanic** or **voltaic cells** store electrical energy, and the net reaction during discharge is called the **spontaneous cell reaction.**
- **Galvanic** cell operates **spontaneously**.
- **Batteries** are usually made from **several galvanic cells connected in series** to produce higher voltages than a single cell can produce.
- **Electrolytic** cell operates by applying external voltage, so it is **non spontaneously.**

For both galvanic and electrolytic cells:

1) **Reduction** always takes place at the **cathode**.
2) **Oxidation** always takes place at the **anode**.
3) **The cathode** in a galvanic cell becomes **the anode,** however, when the cell is operated as an electrolytic cell.
4) Both **Galvanic** and **electrolytic** cell could have **reversible and irreversible** redox reactions.

Representing electrochemical Cells Schematically

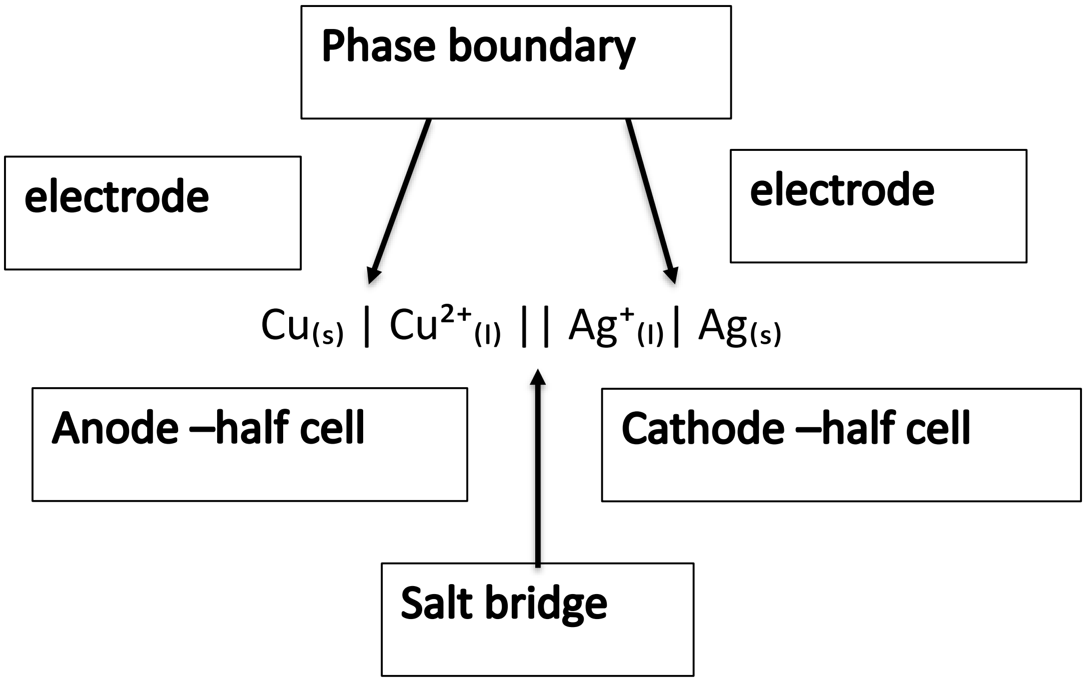
- A schematic (cell notation) is a compact **thermodynamic** and **kinetic description** of an electrochemical system. It tells you :
- Where **oxidation** occurs (**anode**), where desined on the **left**
- Where **reduction** occurs (**cathode**), where desined on the **right**
- The **phases involved** (solid, aqueous, gas)
- The **direction of electron flow**
- Which species control the **electrode potential**

Anode | Anode solution|| cathode solution| cathode

Example1: $2Ag^{+}{}_{(l)} + Cu_{(s)} \leftrightharpoons 2Ag_{(s)} + Cu^{2+}{}_{(l)}$

At cathode: $Ag^{+}{}_{(l)} \leftrightharpoons Ag_{(s)} + e^{-}$

At anode : $Cu_{(s)} \leftrightharpoons Cu^{2+}{}_{(l)} + 2e^{-}$



Cell notation: $Cu_{(s)}$ | $Cu^{2+}{}_{(0.02M)}$ || $Ag^{+}{}_{(0.02M)}$ | $Ag_{(s)}$

Example2: $Cu^{2+}{}_{(l)} + Zn_{(s)} \leftrightharpoons Cu_{(s)} + Zn^{2+}{}_{(l)}$

$Zn_{(s)} \leftrightharpoons Zn^{2+}{}_{(l)} + 2e^-$ (anode) oxidation

$Cu^{2+}{}_{(l)} + 2e^- \leftrightharpoons Cu_{(s)}$ (cathode) reduction

Schematic representation: $Zn_{(s)}|Zn^{2+}{}_{(l)}\ ||\ Cu^{2+}{}_{(l)}|\ Cu_{(s)}$

Example3: Hydrogen reference electrode SHE ?

$$2H^+{}_{(l)} + 2e^- \leftrightharpoons H_{2(aq)}$$

Representation : $Pt|H_{2\ (g\ ,\ 1\ atm)}|\ H^+{}_{(\ aq,\ a=1)}$

- This is **half-cell notation**, **not full-cell notation**
- Platinum is **inert** (just an electron conductor)
- Electrochemical notation always follows: Solid|gas|solution

Example4: **Pt** working electrode **Fe^{3+}/Fe^+** couples vs **Ag/AgCl** reference electrode?

Cell notation: $Pt|Fe^{2+}{}_{(aq)}, Fe^{3+}{}_{(aq)}|\ Ag^+{}_{(aq)}|Ag_{(s)}$

Currents in Electrochemical Cells

During **discharge** of a **galvanic cell, charge is transported** by three mechanisms:

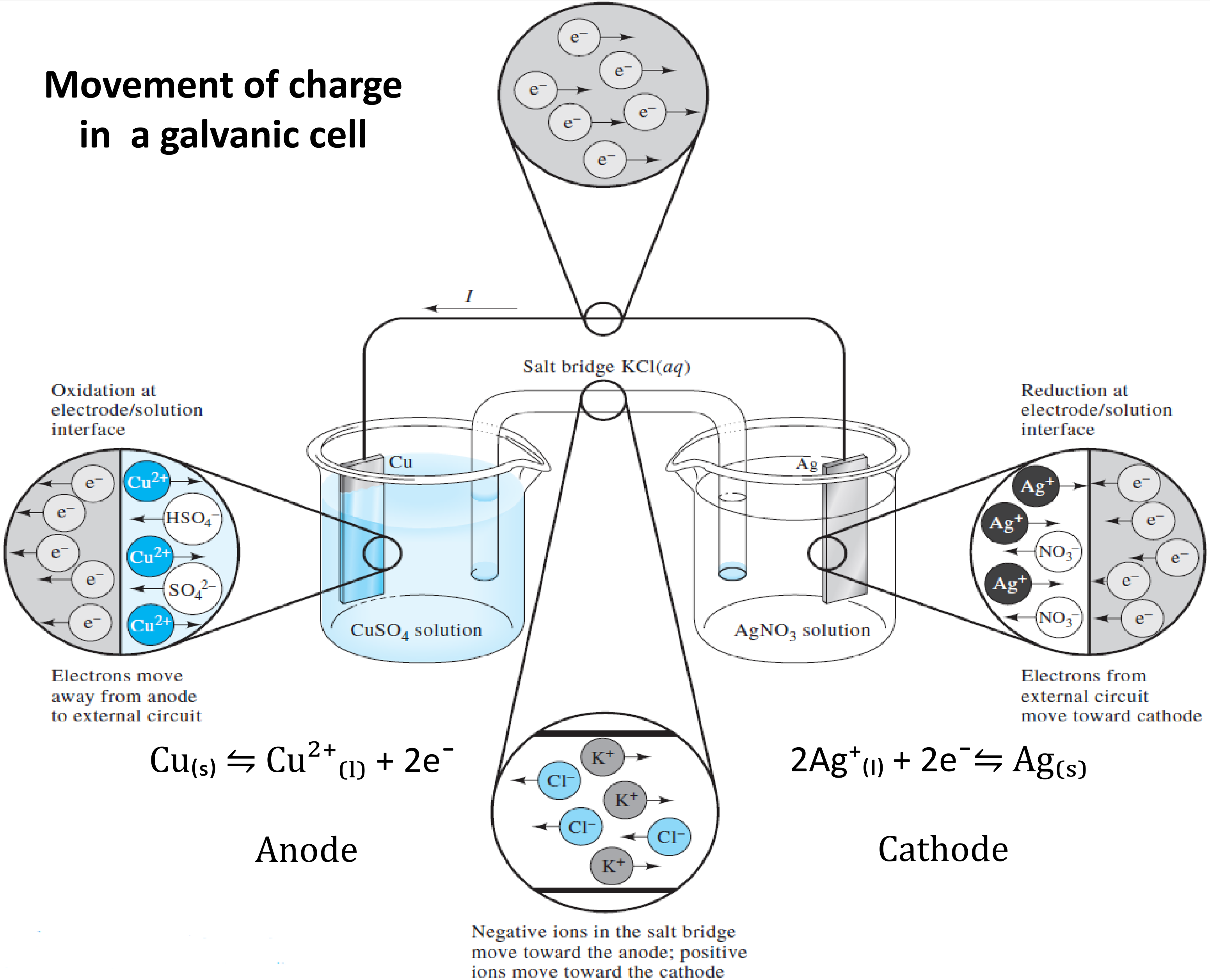
1) Electrons carry charge through the electrodes and external circuit; conventional current (I) flows opposite to electron flow from **anode** to **cathode**.

2) Ions carry charge in the electrolyte:

- At the **anode**, oxidation produces cations to the bulk of solution while anions migrate toward the anode electrode.
- In the salt bridge, anions migrate towards the bulk of anodic solution while cations migrate towards the cathodic bulk solution to maintain electrical neutrality.
- At the **cathode**, cations move toward the electrode to be reduced while anions move away.

3) Redox reactions at the electrodes couple electronic conduction electrodes) with ionic conduction (solution), allowing continuous current flow.

Movement of charge in a galvanic cell



$Cu_{(s)} \leftrightharpoons Cu^{2+}_{(l)} + 2e^-$

Anode

$2Ag^+_{(l)} + 2e^- \leftrightharpoons Ag_{(s)}$

Cathode

References

1.Skoog, D. A., West, D. M., Holler, F. J., & Crouch, S. R. (1996). *Fundamentals of analytical chemistry* (Vol. 33, pp. 53-55). Fort Worth: Saunders College Pub.

2. Christian, G. D., Dasgupta, P. K., & Schug, K. A. (2013). Analytical chemistry. John Wiley & Sons.

3. Skoog, D. A., Holler, F. J., & Crouch, S. R. (2007). *Instrumental analysis* (Vol. 47). Belmont: Brooks/Cole, Cengage Learning.

4. Harris, D. C. (2010). *Quantitative chemical analysis*. Macmillan.