



**RedOx Titration** A volumetric analysis based on a chemical reaction where there is a transfer of electrons from the *reducing agent* to the *oxidizing agent*.

Unlike Acid-Base titration which tracks the movement of protons( $H^+$ ), RedOx titration tracks the movement of **electrons** ( $e^-$ ), resulting in a change in the oxidation state (valence number) of the reacting species.

## Core Principle

### The Fundamental Principle: The "Electron Balance Sheet"

- **Oxidation:** The process of *losing* electrons (Increase in oxidation number).
- **Reduction:** The process of *gaining* electrons (Decrease in oxidation number).

**OIL RIG: Oxidation Is Loss; Reduction Is Gain.**

**LEORA: Loss of Electrons is Oxidation; it is a Reducing Agent**

**GEROA: Gain of Electrons is Reduction; it is an Oxidizing Agent**

### Equivalence point

*The exact point where electrons lost = electrons gained stoichiometrically.*

All analyte has reacted.  
No excess oxidizing or reducing agent yet.

Indicator lights up when there is a negligible excess amount of oxidizing or reducing agent.

## History

Began in 19th century analytical chemistry.

Major milestones:

- 1820s–1840s → Early oxidation studies
- 1850s → Potassium permanganate introduced as titrant
- Late 1800s → Iodometry standardized
- Early 1900s → Cerimetric titrations refined

Redox became popular as:

- It allowed direct measurement of reducing/oxidizing substances
- It was highly sensitive
- It did not always require external indicators

$KMnO_4$  especially became attractive because:

- It is self-indicating (purple to colorless transition)

Originally, redox was adopted for industrial chemistry:

- Iron assays
- Hydrogen peroxide
- Oxalates
- Arsenic

Pharmaceutical Relevance

Pharmacy began formal standardization in the late 1800s to early 1900s, when pharmacopeias became structured.

Redox entered pharmacopeial assays when:

1. Certain drugs had no acid-base character.
2. Some drugs had strong reducing or oxidizing functional groups.
3. Neutralization did not apply.

Examples:

- Ascorbic acid: Strong reducing agent
- Hydrogen peroxide: Oxidizing agent
- Ferrous sulfate: Easily oxidized  $Fe^{2+}$

- Iodine preparations: Redox-based quantification

By early 20th century, redox methods were officially included in pharmacopeias because of the following reasons:

- Selective
- Reproducible
- Suitable for certain functional groups
- Less dependent on solubility in aqueous acid/base

Redox is chosen when:

1. The drug undergoes electron transfer
2. It changes oxidation state
3. It contains functional groups like:
  - Phenols
  - Aldehydes
  - Sulfides
  - $\text{Fe}^{2+}$
  - Iodide
  - Ascorbate

Ascorbic acid is weakly acidic.

But its assay is better done via redox because:

- It is easily oxidized to dehydroascorbic acid.
- Proton transfer is not the main analytical property.
- Electron transfer is the measurable event.

## Techniques

PERMANGANOMETRY	
VS	$\text{KMnO}_4$
1 std	Na oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ )
Indicator	$\text{KMnO}_4$
Direct	$\text{H}_2\text{O}_2$ Ferrous Salts Oxalic acid
Indirect	Calcium gluconate Calcium lactate Malic acid
Residual	Residual Na and K nitrite
Endpoint Purple	Faint Pink

CERIMETRY	
VS	Cerric sulfate
1 std	Arsenic trioxide ( $\text{As}_2\text{O}_3$ )
Indicator	Orthophenanthroline
Direct	Menadione $\text{FeSO}_4$
Indirect	
Residual	
Endpoint Purple	Appearance of Blue/Green

IODIMETRY (DIRECT)	
VS	Standard iodine solution
1 std	Arsenic trioxide ( $\text{As}_2\text{O}_3$ )
Indicator	Starch
Direct	Reducing Agent <ul style="list-style-type: none"> <li>• Ascorbic acid</li> <li>• Na metabisulfite</li> <li>• Na thioglycolate</li> <li>• Iodine tincture</li> </ul>
Principle Reaction	Drug reduces iodine to iodide
Endpoint Purple	Appearance of Blue

IODOMETRY (INDIRECT)	
VS	Standard sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ )
1 std	Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )
Indicator	Starch
Oxidizing Agents	<ul style="list-style-type: none"> <li>• Ferric/cupric salt</li> <li>• Chlorine (<math>\text{NaOCl}</math>)</li> <li>• Phenol</li> <li>• Resorcinol</li> </ul>
Principle Reaction	Drug oxidizes iodide to iodine
Endpoint Purple	Disappearance of Blue