

# pH and ORP Comparisons

Theory

Selection

Maintenance

Applications

## Similarities:

- They are Electrochemical measurements
- They require a special high impedance input circuit
- Both use the same Ag/AgCl reference electrode design



pH



ORP

## Differences:

- pH electrodes respond to hydrogen ion activity
- ORP electrodes respond to oxidizing or reducing activities of ions
- pH electrodes are constructed of hydrogen ion sensitive glass
- ORP electrodes are constructed of a noble metal



Reference

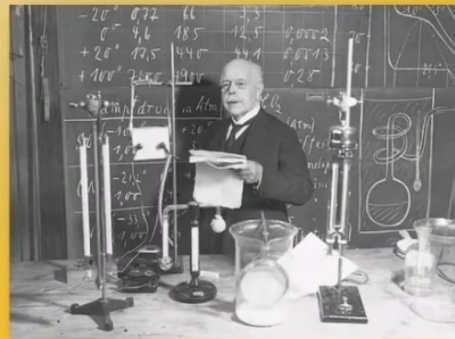
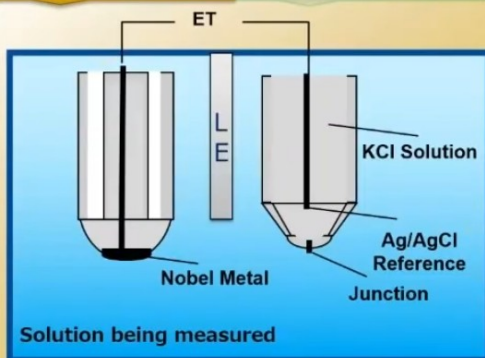
# Working Principle

Theory

Selection

Maintenance

Applications



## Nernst formula:

$$E_h = E^0 + \frac{RT}{nF} \log \frac{A_{ox}}{A_{red}}$$

ORP measures the total activity of all oxidizing ( $A_{ox}$ ) and reducing agents ( $A_{red}$ ) within a solution. It reflects the ratio  $A_{ox}/A_{red}$ .

## Working Principle

### Theory

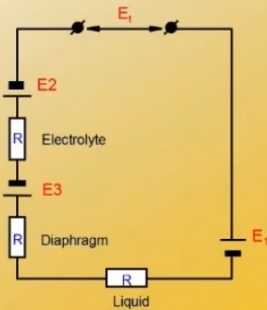
### Selection

### Maintenance

### Applications

#### ■ Nernst formula:

$$■ E_h = E^0 + \frac{RT}{nF} \log \frac{A_{ox}}{A_{red}}$$

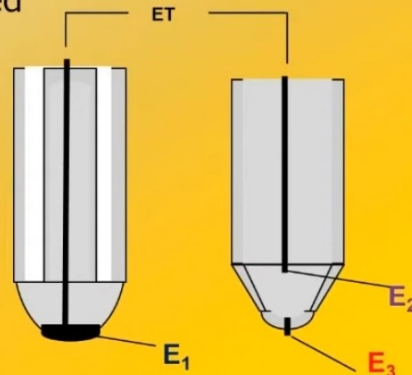


The following are the most significant potentials:

- E1 = Potential between ORP metal surface and the process.
- E2 = Potential between the Ref electrode pin and electrolyte.
- E3 = Potential between interface electrolyte interface and process.

Metal Pin connected to Noble Metal (Gold or Platinum)

Reference Electrode



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Læg mærke til at måling af potentiale sker over en bro mellem pH elektroden (t.h) og ORP proben. Efter min opfattelse er den anførte Nernst ligning ikke i samsvar med moderne notation (tidl. kunne den naturlige logaritme skrives som “log” og titalslogaritmen som “log<sub>10</sub>”)

**Q:** In which fields are ORP (oxidation-reduction potential) probes applicable, and what is the theory behind these applications of the probe?

**A:** **ORP (Oxidation–Reduction Potential) probes** are used wherever it’s important to know how oxidizing or reducing an environment is. They don’t measure specific chemicals directly; instead, they measure the **electrical potential created by all redox-active species in a solution**. Below is a clear breakdown of **where ORP probes are used** and **the theory behind their application**.

## 1. Fields Where ORP Probes Are Applied

### 1. Water and Wastewater Treatment

#### Applications

- Monitoring disinfection efficiency (chlorine, ozone, bromine)

- Controlling biological treatment processes (nitrification/denitrification)
- Detecting anaerobic vs. aerobic conditions

#### **Why ORP is useful**

- High ORP → strong oxidizing conditions (effective disinfection)
  - Low ORP → reducing or anaerobic conditions (needed for denitrification)
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## **2. Drinking Water and Pool/Spa Management**

### **Applications**

- Control of chlorine or bromine dosing
- Ensuring microbial safety

### **Why ORP is useful**

- ORP correlates with the **sanitizing power** of disinfectants better than free chlorine alone
  - Accounts for pH and organic load automatically
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## **3. Environmental Monitoring**

### **Applications**

- Soil and groundwater redox status
- Wetland and sediment studies
- Biogeochemical cycling (iron, sulfur, nitrogen)

### **Why ORP is useful**

- Indicates dominant redox processes (e.g., oxygen reduction, sulfate reduction, methanogenesis)
  - Helps predict contaminant mobility (e.g., arsenic, iron, manganese)
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## **4. Industrial Chemical Processes**

### **Applications**

- Chemical manufacturing
- Corrosion monitoring
- Electroplating and metal finishing

### **Why ORP is useful**

- Ensures correct oxidation state of reactants
  - Prevents unwanted side reactions or corrosion
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## **5. Food and Beverage Industry**

### **Applications**

- Brewing and winemaking
- Fermentation control
- Shelf-life and quality assessment

### **Why ORP is useful**

- Fermentation requires low ORP (reducing conditions)
  - Oxidation negatively affects flavor and stability
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## **6. Pharmaceutical and Biotechnology Processes**

### **Applications**

- Fermentation and cell culture
- Bioreactor control
- Sterility and process consistency

### **Why ORP is useful**

- Cellular metabolism is sensitive to redox conditions
  - Helps maintain reproducible growth environments
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## **7. Aquaculture and Fisheries**

### **Applications**

- Water quality monitoring
- Disease prevention
- Biofilter performance

### **Why ORP is useful**

- Reflects oxygen availability and organic loading
- Early warning of toxic anaerobic conditions

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## 8. Mining and Hydrometallurgy

### Applications

- Heap leaching
- Bioleaching
- Metal recovery processes

### Why ORP is useful

- Metal solubility and recovery depend on redox state
  - Controls oxidation of sulfide minerals
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## 2. Theory Behind ORP Probe Operation

### What ORP Measures

An ORP probe measures the **electrical potential (in millivolts)** between:

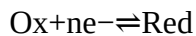
- An **inert measuring electrode** (usually platinum or gold)
- A **reference electrode** (commonly Ag/AgCl or calomel)

This potential reflects the **tendency of the solution to gain or lose electrons.**

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### Electrochemical Basis (Nernst Equation)

For a general redox reaction:



The electrode potential is given by the **Nernst equation**:

$$E = E^\circ + \frac{RT}{nF} \ln \left( \frac{[\text{Ox}]}{[\text{Red}]} \right)$$

Where:

- $E$  = measured ORP
- $E^\circ$  = standard electrode potential

- $R$  = gas constant
- $T$  = temperature
- $n$  = number of electrons transferred
- $F$  = Faraday constant

In real systems, many redox couples contribute simultaneously, so the measured ORP is a **mixed potential**.

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### Interpretation of ORP Values (Typical)

ORP (mV)	Environment
+600 to +800	Strongly oxidizing (ozone, chlorine)
+300 to +500	Aerobic, disinfected water
0 to +200	Weakly oxidizing
-100 to 0	Reducing
-200 to -400	Strongly reducing (anaerobic, sulfide-rich)

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### Why ORP Is a Control Parameter (Not a Concentration)

- ORP responds to **all oxidants and reductants simultaneously**
  - Automatically incorporates effects of:
    - pH
    - Temperature
    - Organic matter
    - Interfering species
  - This makes ORP especially valuable for **process control**, even when exact chemistry is complex.
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## 3. Summary

- **ORP probes are widely used** in water treatment, environmental science, industry, food production, biotechnology, and mining.
- **They measure electron activity**, not individual chemicals.
- The underlying theory is classical electrochemistry, governed by the **Nernst equation**.
- ORP is best used as an **indicator of redox conditions and process effectiveness**, rather than a precise analytical measurement.

If you'd like, I can also explain **how ORP differs from dissolved oxygen, how to calibrate ORP probes, or how to interpret ORP in a specific application.**

**Q: Yes, please suggest read out values of the probe from seabed sediments exposed to an anoxic event due to decomposition of organic material at the time the sediments was laid down**

A: In seabed sediments that experienced an **anoxic event caused by intense decomposition of organic matter at the time of deposition**, ORP (Eh) values are typically **strongly negative** and follow a predictable redox sequence with depth. Below are **realistic ORP read-out ranges**, tied directly to the **biogeochemical processes** occurring in such sediments.

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## **1. Expected ORP (Eh) Values in Anoxic Marine Sediments**

### **Surface or Slightly Buried Layer (Immediately After Deposition)**

If oxygen was rapidly consumed:

- **ORP: 0 to –100 mV**
  - **Conditions:** Suboxic → onset of anaerobic metabolism
  - **Dominant processes:**
    - Oxygen depletion
    - Nitrate reduction (denitrification)
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### **Shallow Anoxic Zone (Organic-Rich Sediments)**

Once nitrate is exhausted:

- **ORP: –100 to –200 mV**
  - **Conditions:** Anoxic, mildly reducing
  - **Dominant processes:**
    - Manganese (IV) reduction
    - Iron (III) reduction
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### **Fully Developed Anoxia (Typical for Black, Organic-Rich Mud)**

With continued organic matter decay:

- **ORP: –200 to –300 mV**

- **Conditions:** Strongly reducing
- **Dominant processes:**
  - Sulfate reduction (very common in marine settings)
  - Formation of H<sub>2</sub>S and metal sulfides (e.g., pyrite precursors)

## Extreme Reducing Conditions (Euxinic / Methanogenic)

In highly organic sediments with prolonged stagnation:

- **ORP:** -300 to -450 mV
- **Conditions:** Severely reducing
- **Dominant processes:**
  - Methanogenesis
  - Abundant free sulfide
  - Black laminated sediments, framboidal pyrite

## 2. Typical ORP Profile With Depth (Marine Sediment Column)

Depth Below Seafloor	ORP (mV)	Dominant Redox Process
Sediment–water interface	+50 to -50	Oxygen → nitrate reduction
1–5 cm	-100 to -200	Mn / Fe reduction
5–20 cm	-200 to -300	Sulfate reduction
>20 cm	-300 to -450	Methanogenesis

*(Actual depths depend on organic loading, sedimentation rate, and bioturbation.)*

## 3. Why These Values Occur (Theory Linked to Decomposition)

### Redox Ladder (Terminal Electron Acceptors)

As organic matter decomposes, microbes sequentially use electron acceptors in order of decreasing energy yield:

1. O<sub>2</sub> → H<sub>2</sub>O
2. NO<sub>3</sub><sup>-</sup> → N<sub>2</sub>
3. Mn(IV) → Mn(II)
4. Fe(III) → Fe(II)
5. SO<sub>4</sub><sup>2-</sup> → H<sub>2</sub>S

6.  $\text{CO}_2 \rightarrow \text{CH}_4$

Each step lowers the sediment's **electron activity**, producing increasingly negative ORP readings.

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## 4. Important Practical Notes on ORP Measurements in Sediments

### Probe Behavior in Sediments

- ORP electrodes measure a **mixed potential**, dominated by the most electroactive redox couples (often  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{HS}^-/\text{SO}_4^{2-}$ ).
  - Sulfide strongly drives ORP negative and stabilizes low readings.
  - Values may stabilize slowly (minutes to hours) in fine-grained muds.
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### Reference Electrode Considerations

Reported ORP depends on reference electrode:

- Ag/AgCl → typical modern field probes
- To convert to **Eh vs. SHE**, add:
  - **+200 mV** (approx., temperature dependent)

Example:

Measured  $-250 \text{ mV (Ag/AgCl)} \approx -50 \text{ mV vs. SHE}$

(Always state reference type in publications.)

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## 5. Geological Interpretation

For sediments laid down during an anoxic event:

- **Consistent ORP  $< -200 \text{ mV}$**  → deposition under persistent anoxia
  - **ORP  $< -300 \text{ mV}$**  → euxinic or methanogenic bottom waters
  - Associated indicators:
    - Laminated sediments (no bioturbation)
    - High TOC
    - Pyrite, framboids
    - Elevated Mo, U, V enrichments
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## 6. Summary (Key Takeaways)

- Expect **-200 to -450 mV ORP** in organic-rich, anoxically deposited seabed sediments.
- Values reflect **microbial decomposition pathways**, not a single chemical species.
- Sulfate reduction and methanogenesis dominate marine anoxic sediments.
- ORP profiles provide strong evidence for **paleo-redox conditions** when combined with sedimentology and geochemistry.

If you'd like, I can:

- Convert these ORP values into **paleoenvironmental classifications**
- Compare **marine vs lacustrine anoxic sediments**
- Discuss **limitations of ORP for paleo-records** and how geochemists work around them

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