Theory of Liquid Measurements

- Conductivity/Resistivity
- pH
- ORP
Ionic Conductance
Cell Constant

Conductivity Cell Constant = \frac{\text{Length}}{\text{Area}} = \frac{1 \text{ cm}}{1 \text{ cm}^2} = 1 \text{ cm}^{-1}
Other Cell Constants

Cell Constant = Multiplier
Resistivity/Conductivity Cell

Concentric Electrodes

OUTER ELECTRODE

INNER ELECTRODE

INSULATOR
<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance</td>
<td>ohm</td>
</tr>
<tr>
<td>Conductance</td>
<td>mho, siemens = 1/ohm</td>
</tr>
<tr>
<td>Resistivity</td>
<td>ohm-cm,</td>
</tr>
<tr>
<td></td>
<td>megohm-cm, MΩ-cm</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mho/cm,</td>
</tr>
<tr>
<td></td>
<td>μmho/cm</td>
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<tr>
<td></td>
<td>siemens/cm,</td>
</tr>
<tr>
<td></td>
<td>microsiemens/cm, µS/cm</td>
</tr>
</tbody>
</table>
Units of Conductivity/Resistivity

Industry Preferences:

Resistivity - Semiconductor ultrapure water

Conductivity - Power, Pharmaceutical, Pretreatment stages, Cooling towers, Wastewater

Total Dissolved Solids (ppm TDS)
Cell Constant Traceability

- ASTM D1125 Primary Standard and Pure Water at 15, 25, 40°C
- Standards Lab Cell Constant
- Production Cell Constant
Ultrapure Water Sensor Calibration/ Certification System
## Conductivity, Resistivity, TDS Ranges

Conductivity and resistivity are measured at 25°C; TDS is expressed as Sodium Chloride (NaCl).

<table>
<thead>
<tr>
<th>Resistivity (ohm-cm)</th>
<th>100M</th>
<th>10M</th>
<th>1M</th>
<th>100K</th>
<th>10K</th>
<th>1K</th>
<th>100</th>
<th>10</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrapure water</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Deionized water</td>
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<tr>
<td>Distilled water</td>
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<tr>
<td>Condensate</td>
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<td></td>
<td></td>
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<tr>
<td>Drinking water</td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td>Cooling tower water</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Percentage of acids, bases and salt</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste water</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>Brackish water, Sea water</td>
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<td></td>
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<tr>
<td>Water for Industrial Process</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>5% Salinity</td>
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<td></td>
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<td>2% NaOH</td>
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<td></td>
</tr>
<tr>
<td>20% HCl</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conductivity (µS-cm)</th>
<th>TDS (ppm)</th>
<th>0.01</th>
<th>.1</th>
<th>1</th>
<th>10</th>
<th>100</th>
<th>1000</th>
<th>10k</th>
<th>100k</th>
<th>1000k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.021</td>
<td>0.4</td>
<td>4.6</td>
<td>46</td>
<td>460</td>
<td>4.6k</td>
<td>100k</td>
<td>1000k</td>
<td></td>
</tr>
</tbody>
</table>
On-Line Conductivity Sensor
Calibration/Verification

- On-line instrument
- In-line cell
- Sample take-off
- Process flow
- 200-500 mL/min sample flow
- Flow chamber
- Factory-certified reference cell
- To drain
- Calibrated reference instrument
Temperature Effects on Conductivity
Conductivity/Resistivity Temperature Coefficients

Natural waters, etc.
(>2 µS/cm) ~ 2 %/°C

High purity water
(0.055 µS/cm or 18.2 Megohm-cm) 4 - 7 %/°C
Dissociation of Water

H₂O ⇌ H⁺ + OH⁻
Conductivity vs. Temperature

Conductivity (µS/cm) vs. Temperature (°C) for different NaCl concentrations.
Temperature Compensation

- Standard -- high purity water with mineral contamination
- Linear, %/°C -- special applications with known coefficient
- Cation/Ammonia/ETA -- power plant cycle chemistry and semiconductor acid etch rinse operations
- Alcohol -- special semiconductor rinse operations
- Glycol -- semiconductor coolant monitoring
- Light 84 -- same as Standard but with 1984 pure water data (reads slightly higher resistivity)
- Direct % Concentration Readout of HCl, H₂SO₄, NaOH automatically selects appropriate compensation
Recommended Cell Installation...

Flow should be directed at the end of the sensor
High Conductivity Measurements

- **Applications**
  - Reverse Osmosis feedwater
  - Acid/Base deionizer regenerant concentration
  - Process fluids
  - Recycle water
  - Wastewater/effluent
  - Cooling towers

- **Conductivity Measurement Technologies**
  - Two-electrode contact
  - Four-electrode contact
  - Inductive (non-contact, electrodeless, toroidal)
Conductivity vs. Concentration

Concentration (% by weight)

Conductivity (S/cm)

HCl

H2SO4

NaOH

NaCl
Two-Electrode Conductivity Measurement

50/cm Constant Cell

Graphite Electrodes

Bottom view
Two-Electrode Conductivity Measurement

10/cm Constant Cell

Sheath
Slot
RTD
Graphite Electrodes

Bottom view
Four-Electrode Conductivity Measurement

Four-Electrode Measuring Instrument

AC Current Source

AC Voltage Measurement

Measuring Electrodes

Four Electrode Sensor

Drive Electrodes
Four-electrode sensors and instruments can tolerate poor measuring conditions due to three factors:

1. Electrode metal surface condition is less important.

2. Electrode fouling or coating has much less effect.

3. Four-electrode sensors do not have the narrow channels of high, two-electrode cell constants. The resulting flat surface design is much less vulnerable to fouling.
Inductive Conductivity Measurement

Inductive (non-contact, electrodeless, toroidal) Conductivity Sensor
Inductive Conductivity Measurement

- Virtually non-fouling
- No metal/solution contact
- Reliable high conductivity measurements
- Relatively large sensor size
- Cell constant can be affected by surrounding pipe
### pH Range

<table>
<thead>
<tr>
<th>Acidity</th>
<th>Alkalinity</th>
<th>pH</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extreme</td>
<td>Extreme</td>
<td>14.0</td>
<td>Household bleach</td>
</tr>
<tr>
<td>Very Strong</td>
<td>Strong</td>
<td>13.0</td>
<td>Bleach</td>
</tr>
<tr>
<td>Very Strong</td>
<td>Moderate</td>
<td>12.0</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Very Strong</td>
<td>Moderate</td>
<td>11.0</td>
<td>Milk of magnesia</td>
</tr>
<tr>
<td>Very Strong</td>
<td>Slight</td>
<td>10.0</td>
<td>Borax</td>
</tr>
<tr>
<td>Strong</td>
<td>Moderate</td>
<td>9.0</td>
<td>Baking soda</td>
</tr>
<tr>
<td>Strong</td>
<td>Slight</td>
<td>8.0</td>
<td>Sea water</td>
</tr>
<tr>
<td>Strong</td>
<td>Slight</td>
<td>7.0</td>
<td>Blood</td>
</tr>
<tr>
<td>Moderate</td>
<td>Moderate</td>
<td>6.0</td>
<td>Distilled water</td>
</tr>
<tr>
<td>Moderate</td>
<td>Strong</td>
<td>5.0</td>
<td>Milk</td>
</tr>
<tr>
<td>Moderate</td>
<td>Very Strong</td>
<td>4.0</td>
<td>Corn</td>
</tr>
<tr>
<td>Strong</td>
<td>Very Strong</td>
<td>3.0</td>
<td>Boric acid</td>
</tr>
<tr>
<td>Strong</td>
<td>Extreme</td>
<td>2.0</td>
<td>Orange juice</td>
</tr>
<tr>
<td>Strong</td>
<td>Extreme</td>
<td>1.0</td>
<td>Vinegar</td>
</tr>
<tr>
<td>Strong</td>
<td>Extreme</td>
<td>0.0</td>
<td>Battery acid</td>
</tr>
</tbody>
</table>
**pH Measurement**

Dissociation of water

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

\[ K_w = [\text{H}^+] [\text{OH}^-] \]
**pH Scale**

\[ \text{pH} \sim -\log_{10} [H^+] \]

\[ [H^+] \sim 10^{-\text{pH}} \]

at 25°C
Conductivity vs pH

- Conductivity: 0.055 µS/cm, 18.2 MΩ·cm
- pH: 7
- Acid and Base regions

THORNTON / METTLER TOLEDO
Conductivity vs pH

(Courtesy EPRI, NP-35891)
pH vs. Temperature for Pure Waters

Temperature (°C)

pH

6 7 8 9 10 11

0 10 20 30 40 50 60 70 80 90 100

Pure Water

0.5 ppm NH3

THORNTON / METTLER TOLEDO
Combination pH Electrode

- Measuring membrane
- Reference junction
- RTD (insulated)
- Electrolyte
pH Electrode Output

- Temperature: 0°C, 25°C, 50°C, 100°C
- pH Range: 0 to 14
- mV Range: -400 to 400
pH Temperature Compensation

Electrode mV → \( pH_T \) → Solution Temperature Compensation → \( pH_{25°C} \)

Temperature

Nernst Electrode Temperature Compensation

Adder (standardize offset, asymmetry) Multiplier (slope)

Solution Temperature Coefficient
Detachable pH Electrode System

VP Preamplifier
VP pH Electrode
Housing
High Purity pH Sensor Assembly

- Preamp
- Electrolyte Reservoir
- Combination pH Electrode
- Buffer solution
- Calibration Funnel
- 3-way Valve
- Sample Inlet
- RTD
- to drain
pH Standards

- NIST standards--materials to make up buffers at: 1.681, 3.557, 4.006, 6.863, 7.41, 9.180, 10.011, 12.46 pH

- Commercial standard buffer solutions
  - NIST recipes
  - Integral pH values

- Have unique temperature dependence
High Purity pH Measurement Equipment

- Low volume, stainless steel flow chamber
- Low sample flowrate with atmospheric discharge
- Flowing junction reference electrode
- \textit{Solution} temperature compensation as well as \textit{electrode} temperature compensation
- Convenient disabling of Solution temperature compensation during buffer calibration
- NIST-traceable buffer solutions
**ORP: Oxidation-Reduction (redox) Potential**

- Oxidation-reduction chemical reactions
  - Oxidation—loss of electrons, higher potential
  - Reduction—gain of electrons, reduced potential

- Examples
  - Chlorine, ozone, permanganate can oxidize organics (color, odor, bacteria)
  - Bisulfite or carbon beds can reduce chlorine (protect RO membranes & DI resins); Hydrazine can reduce oxygen

- ORP monitors the status of these reactions
ORP Response to Dechlorination

Dechlorination ORP Titration
Sulfite Addition to Chlorinated Water

ORP (mV)

Volume sodium bisulfite solution (mL)
ORP Electrode System

- Measuring
- Reference
- Platinum Disk
- Reference Junction
- To Measuring Circuit