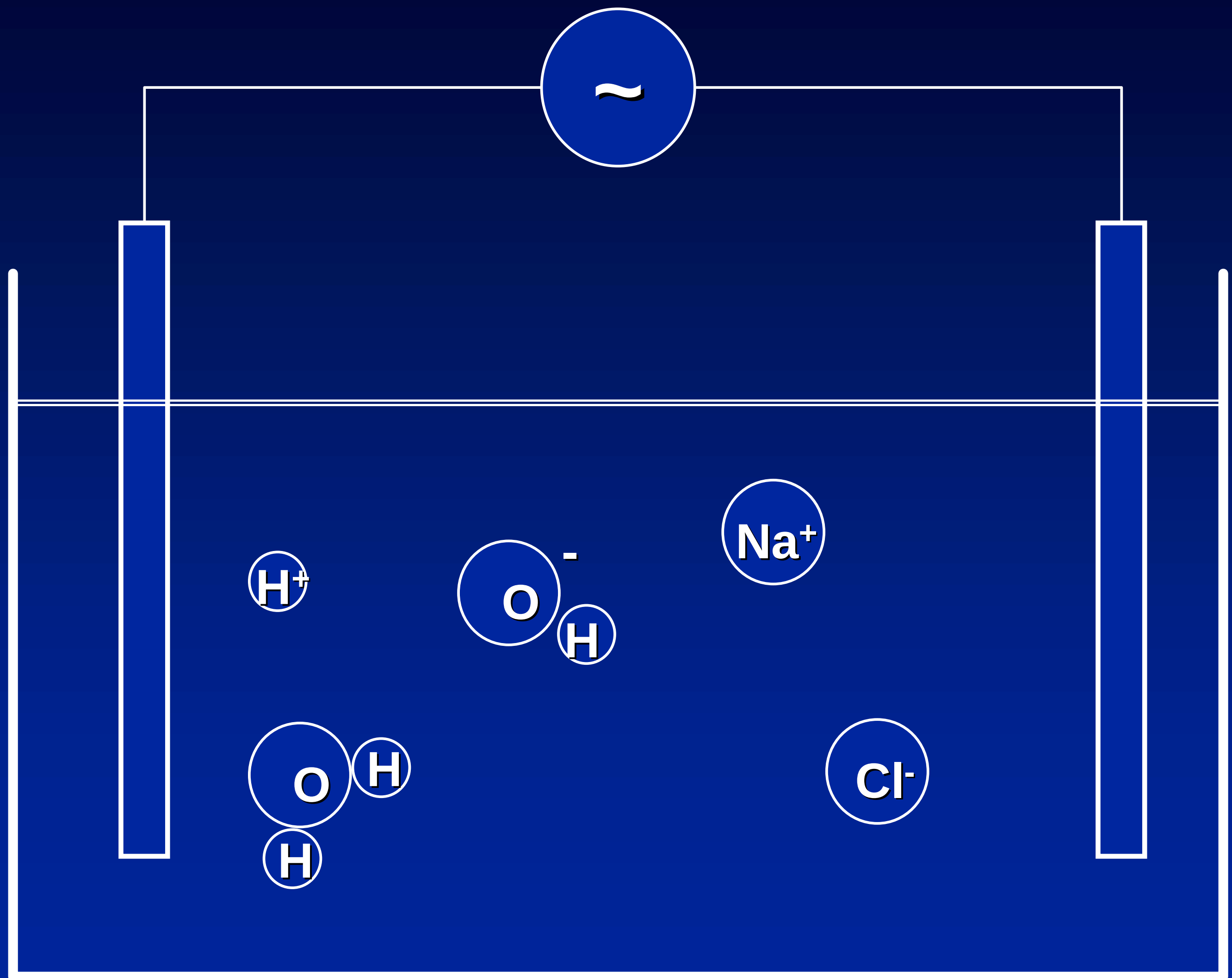
Theory of Liquid Measurements

- ***Conductivity/Resistivity***
- ***pH***
- ***ORP***

Ionic Conductance



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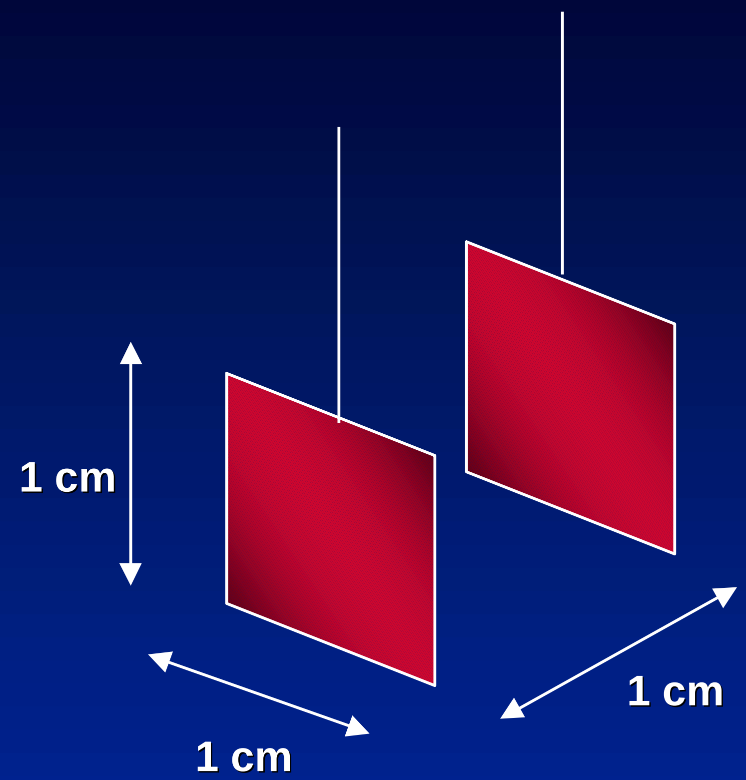
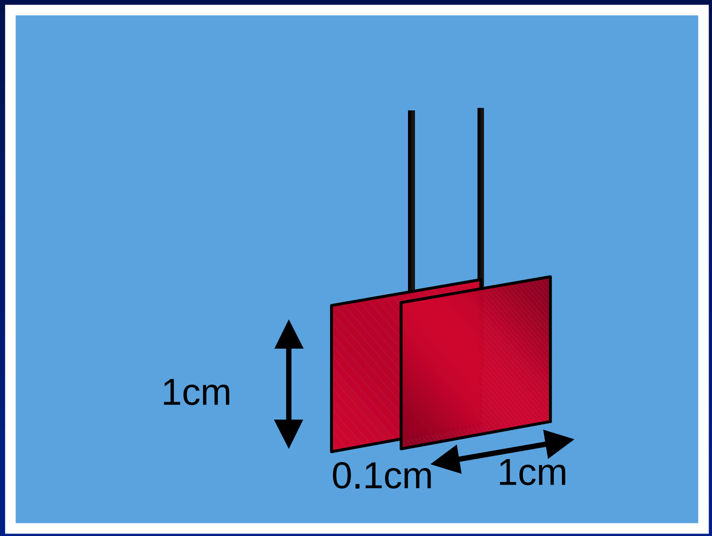
Cell Constant

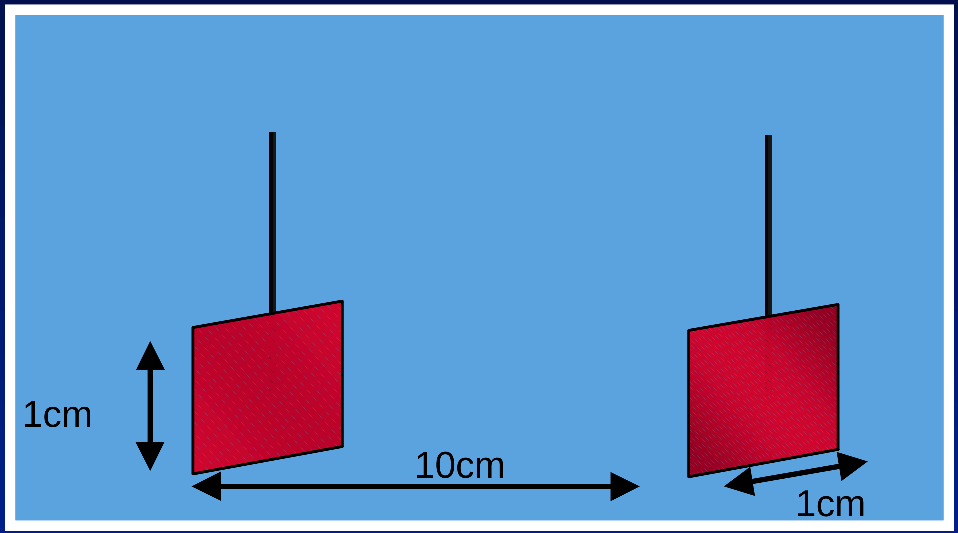


Conductivity Cell Constant $= \dfrac{\text{Length}}{\text{Area}} = \dfrac{1\ \text{cm}}{1\ \text{cm}^2} = 1\ \text{cm}^{-1}$

Other Cell Constants



0.1 constant

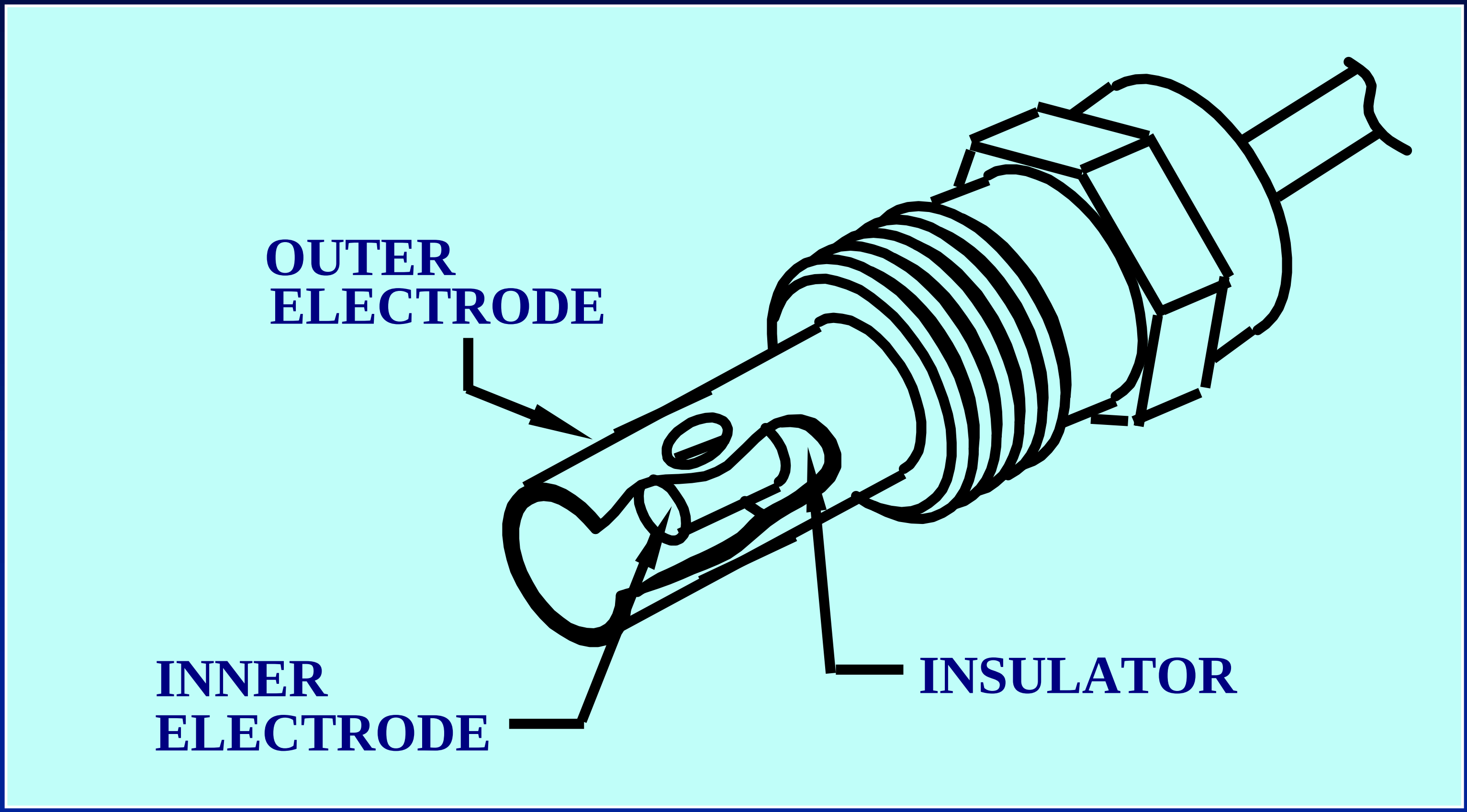


10.0 constant

Cell Constant = Multiplier

Resistivity/Conductivity Cell

Concentric Electrodes



Units of Conductivity/Resistivity

Resistance	**ohm**
Conductance	**mho, siemens = 1/ohm**
Resistivity	**ohm-cm,** **megohm-cm, MΩ-cm**
Conductivity	**mho/cm,** **μmho/cm** **siemens/cm,** **microsiemens/cm, μS/cm**

Units of Conductivity/Resistivity

Industry Preferences:

Resistivity - Semiconductor ultrapure water

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

Total Dissolved Solids (ppm TDS)

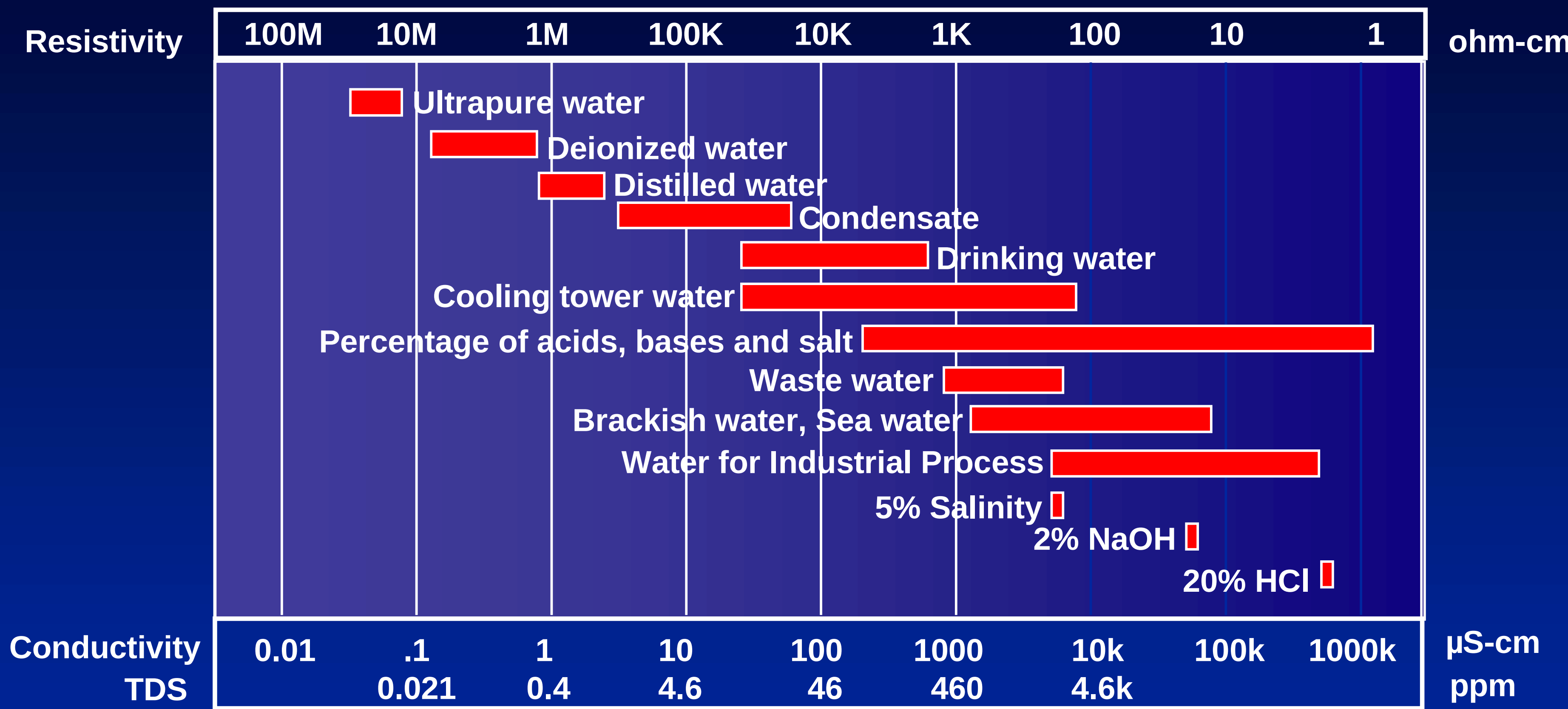
Cell Constant Traceability

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

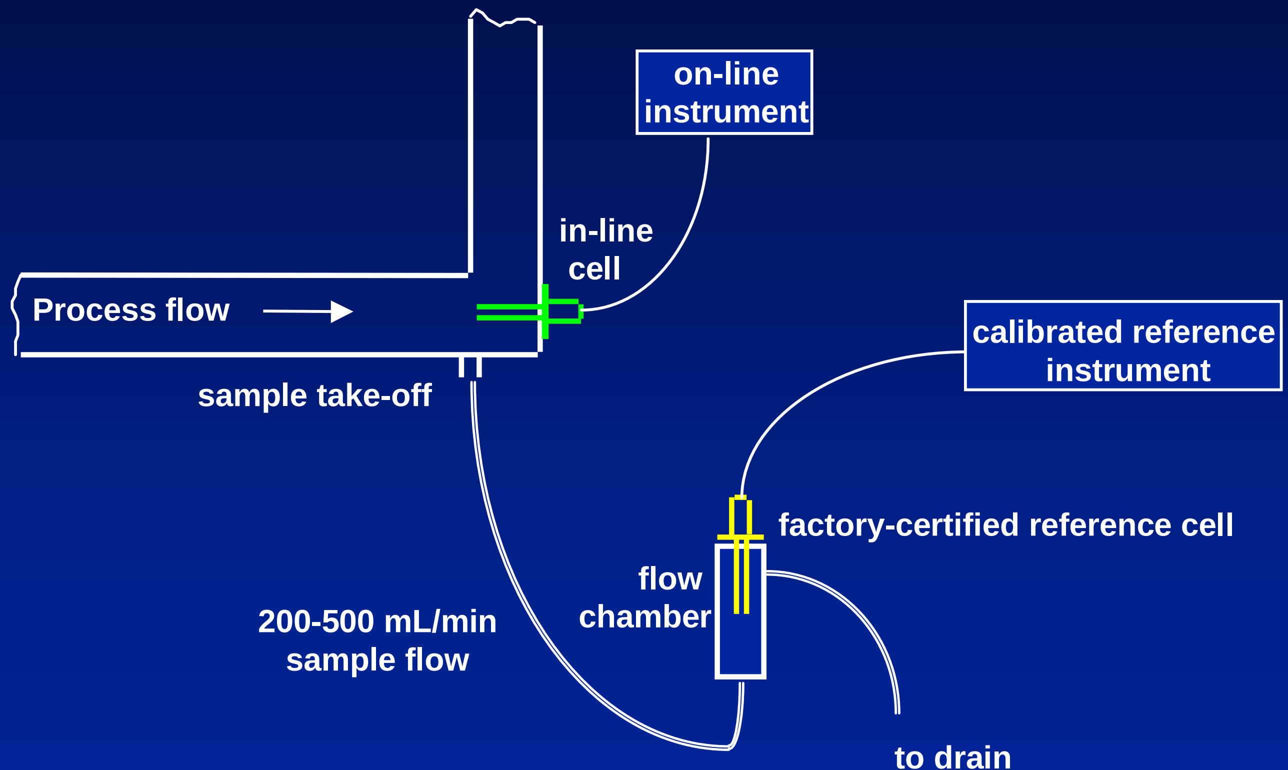
Thornton Inc.

Conductivity, Resistivity, TDS Ranges

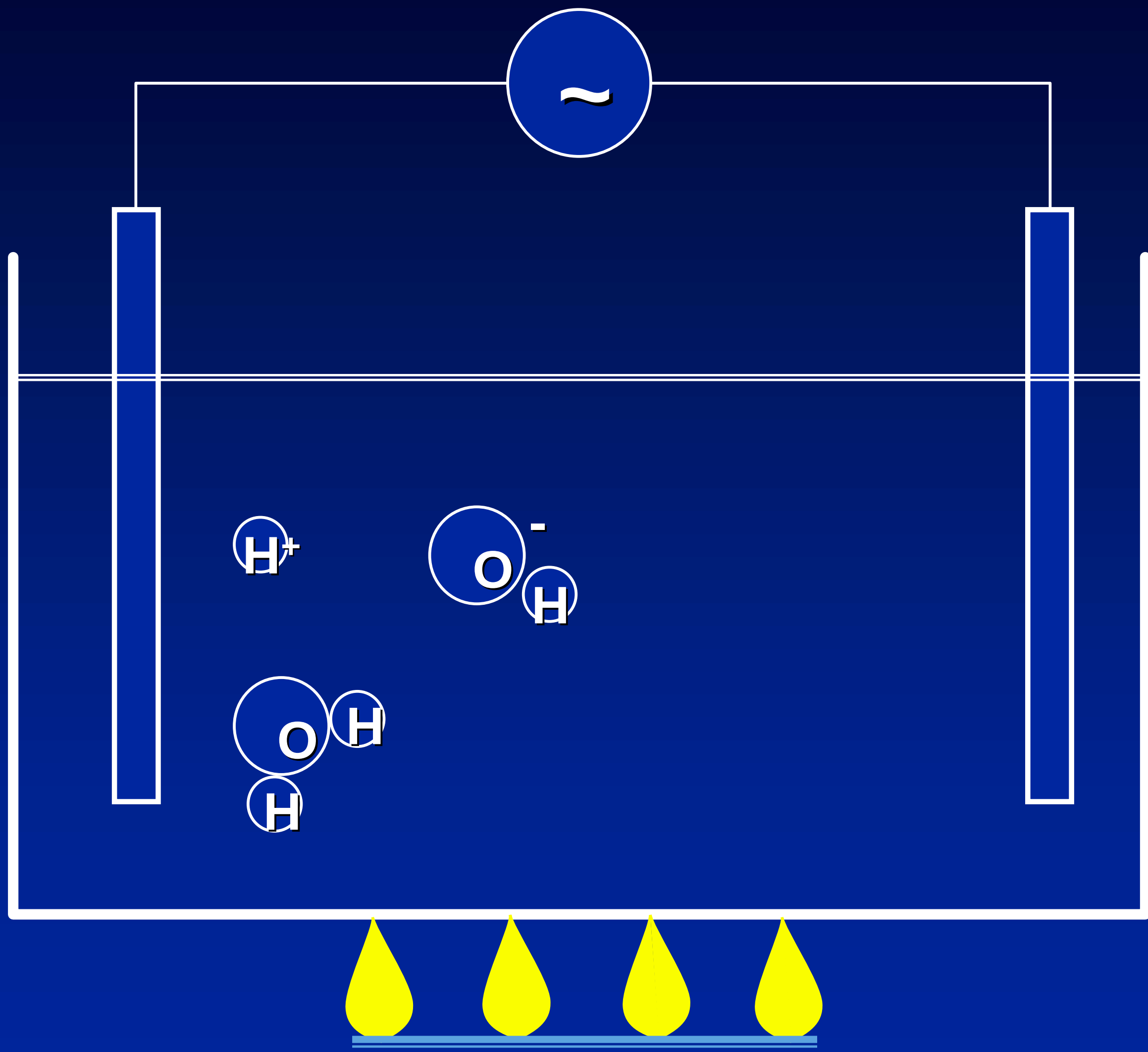


Conductivity and resistivity are measured at 25°C; TDS is expressed as Sodium Chloride (NaCl)

On-Line Conductivity Sensor Calibration/Verification



Temperature Effects on Conductivity



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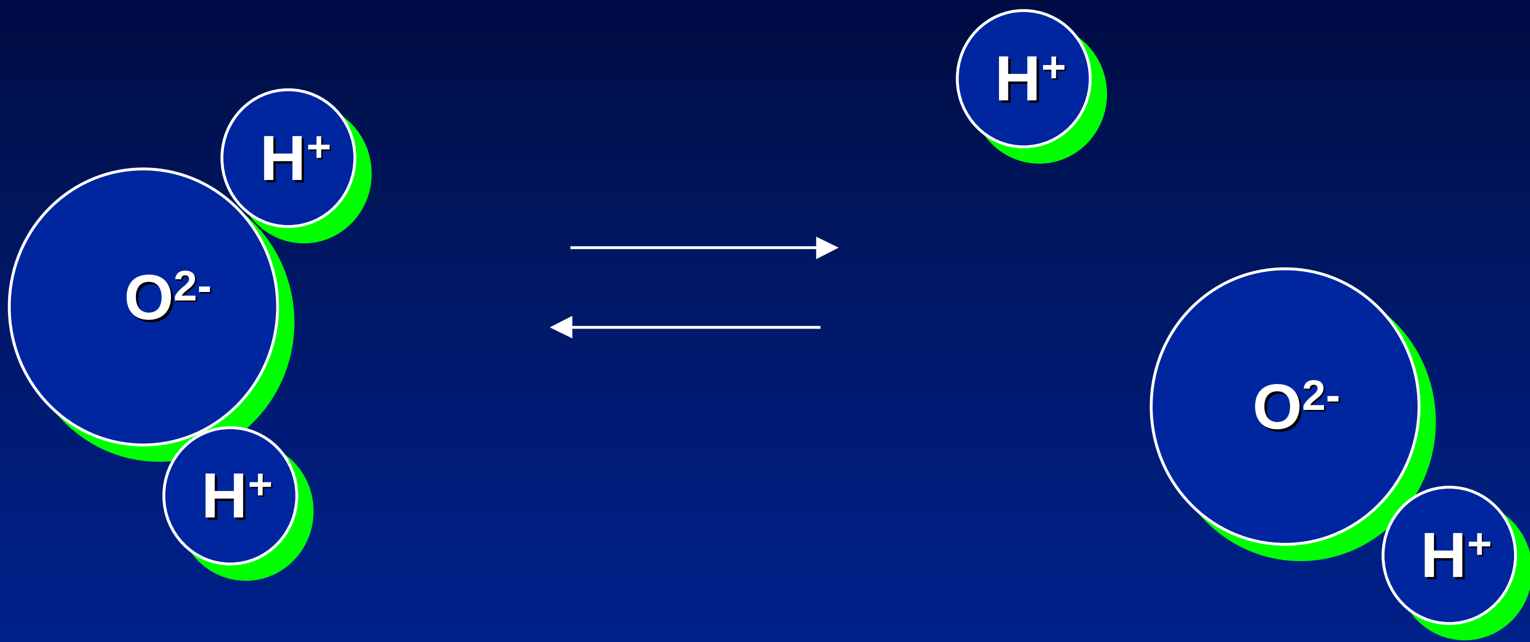
Conductivity/Resistivity Temperature Coefficients

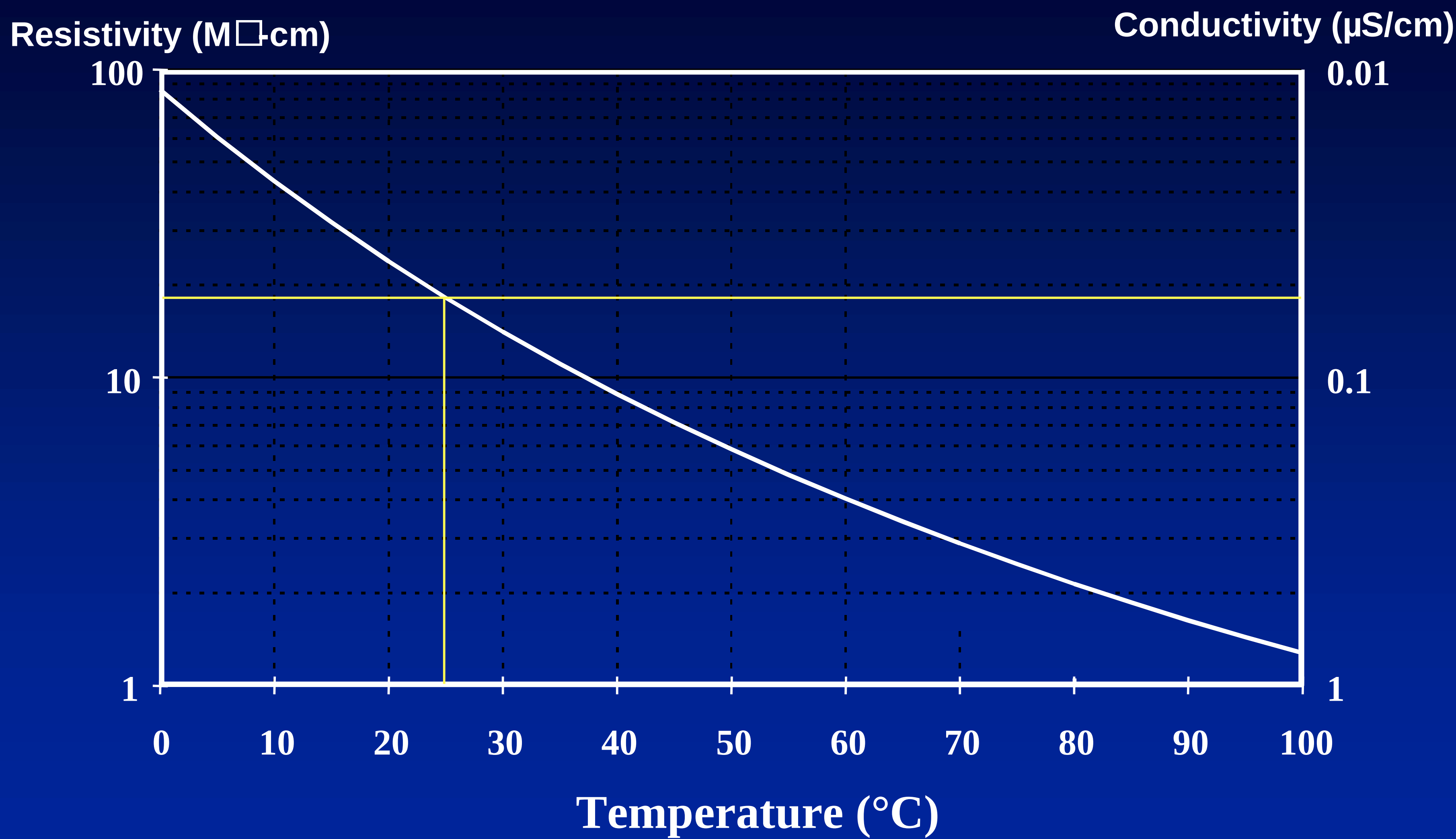
Natural waters, etc.	
(>2 μS/cm)	**~ 2 %/°C**
High purity water	
(0.055 μS/cm or 18.2 Megohm-cm)	**4 - 7 %/°C**

Dissociation of Water



$$H_2O \rightleftharpoons H^+ + OH^-$$

Conductivity of Pure Water vs. Temperature



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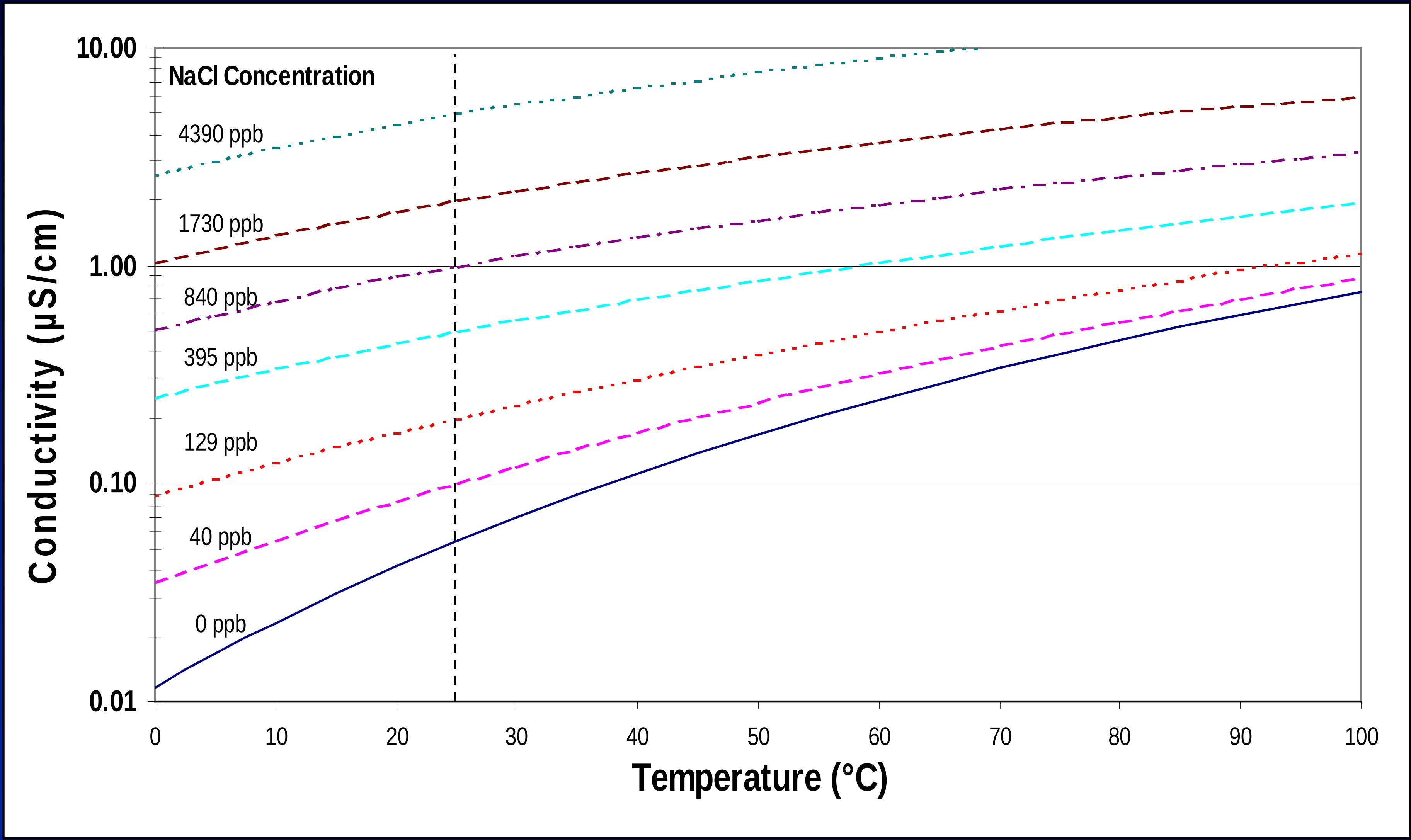
Conductivity vs. Temperature

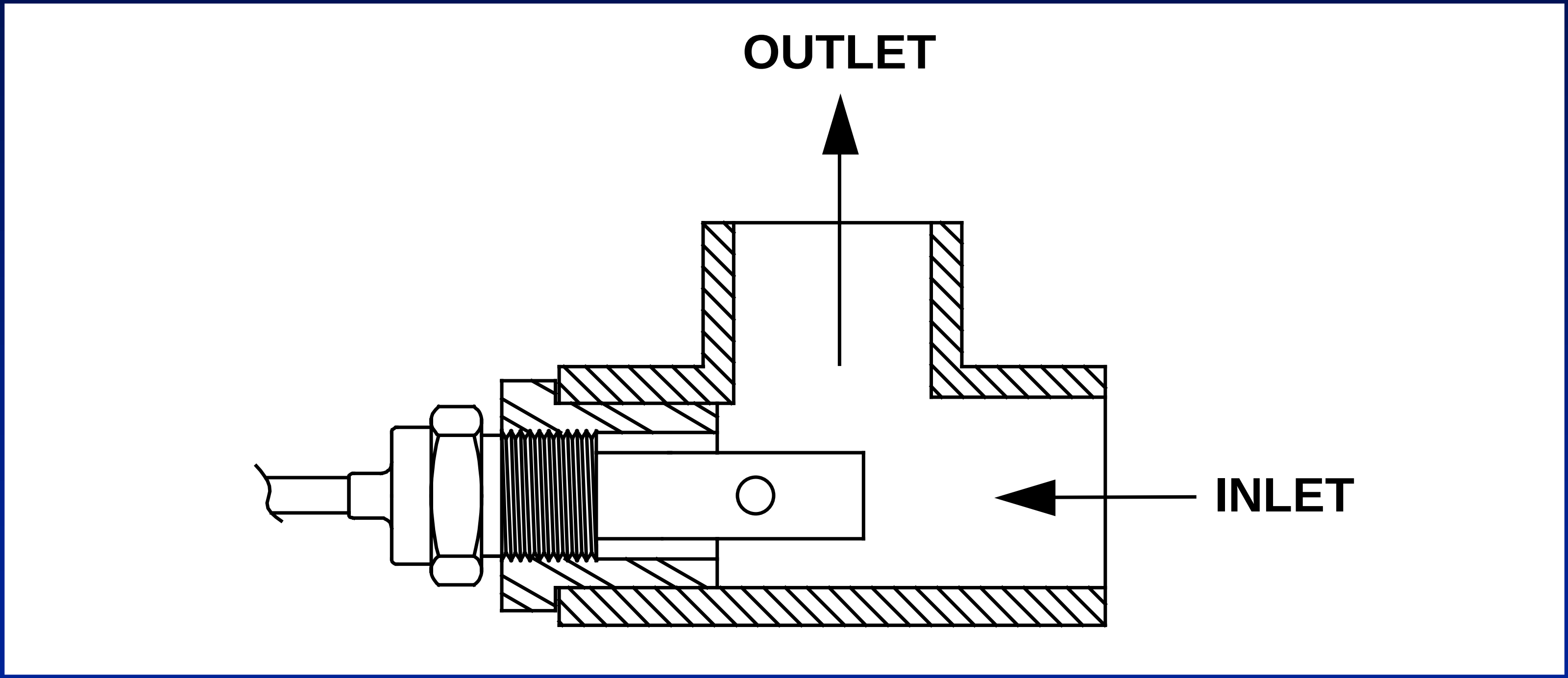


Temperature Compensation

- **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, H_2SO_4, NaOH automatically selects appropriate compensation**

Cell Installation

Recommended Cell Installation...



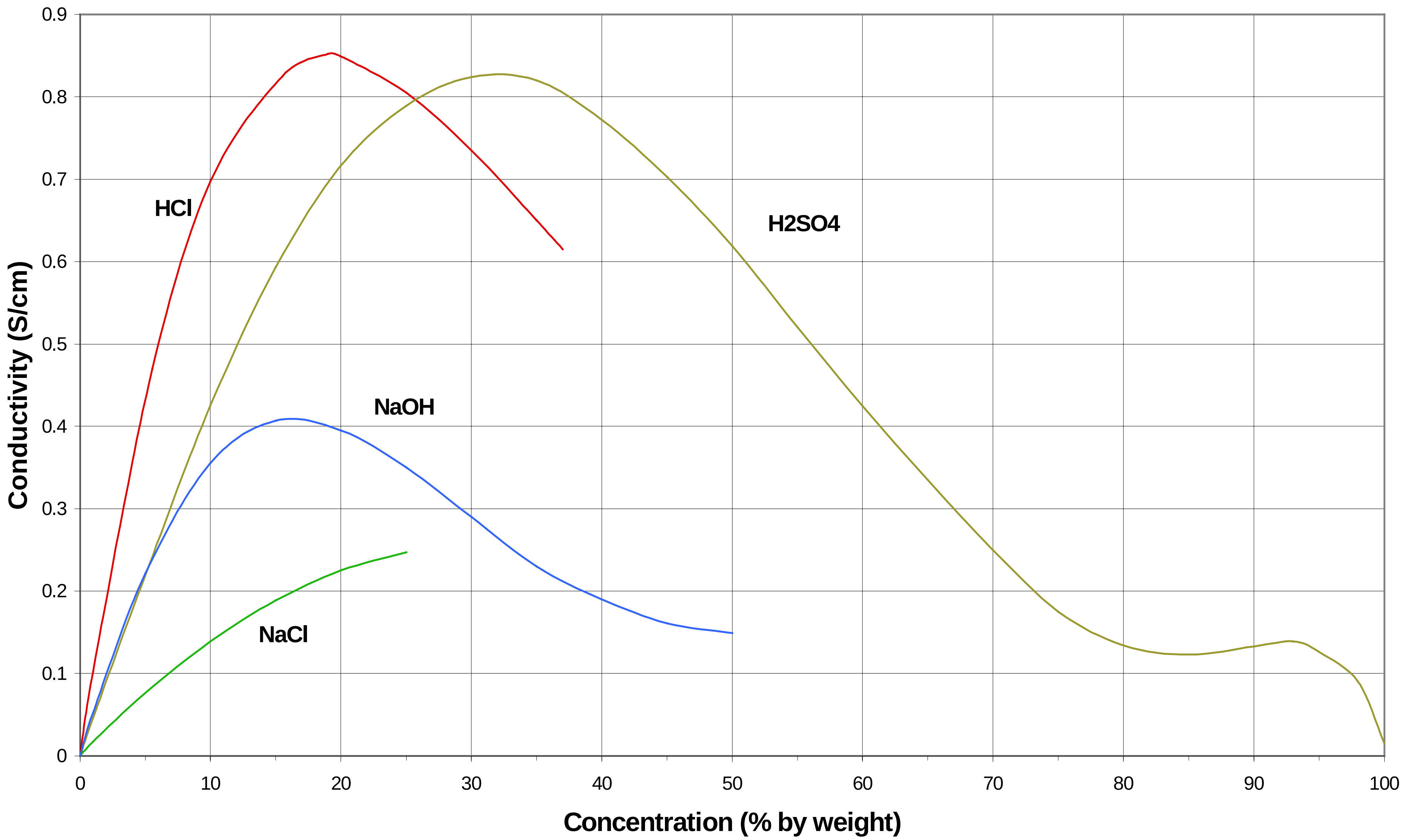
Flow should be directed at the end of the sensor

High Conductivity Measurements

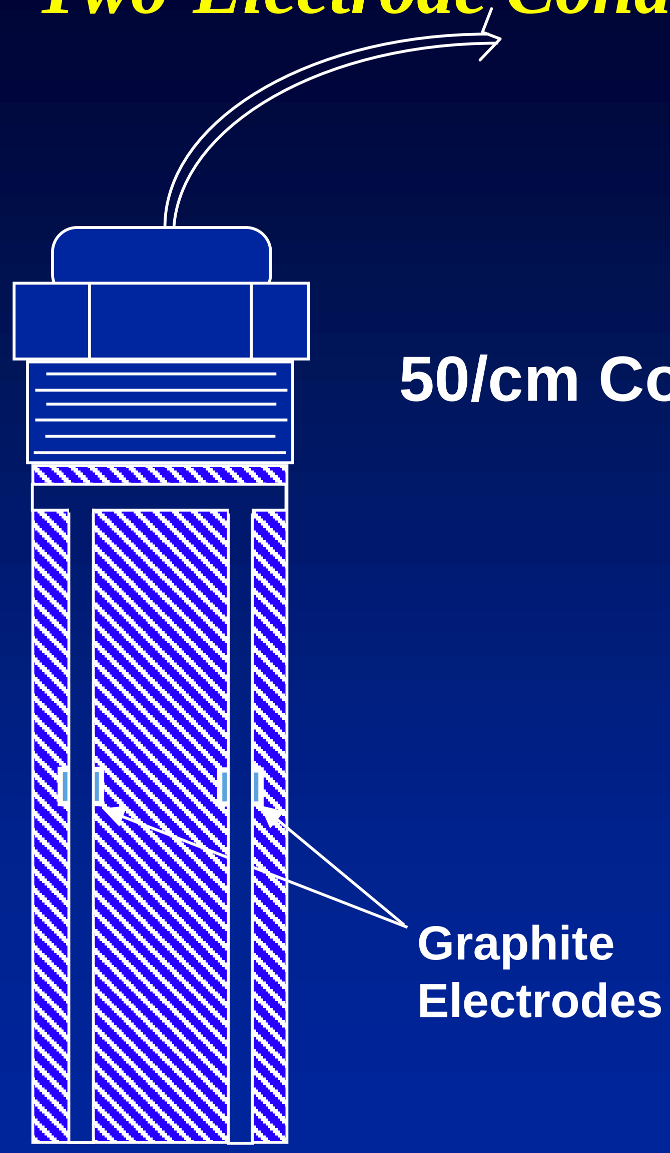
- **Applications**
  - **Reverse Osmosis feedwater**
  - **Acid/Base deionizer regenerant concentration**
  - **Process fluids**
  - **Recycle water**
  - **Wastewater/effluent**
  - **Cooling towers**

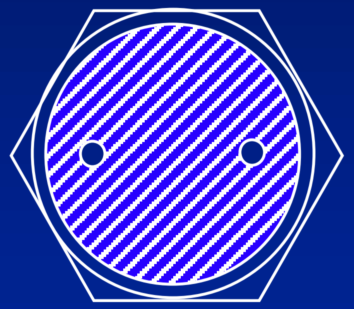
- **Conductivity Measurement Technologies**
  - **Two-electrode contact**
  - **Four-electrode contact**
  - **Inductive (non-contact, electrodeless, toroidal)**

Conductivity vs. Concentration

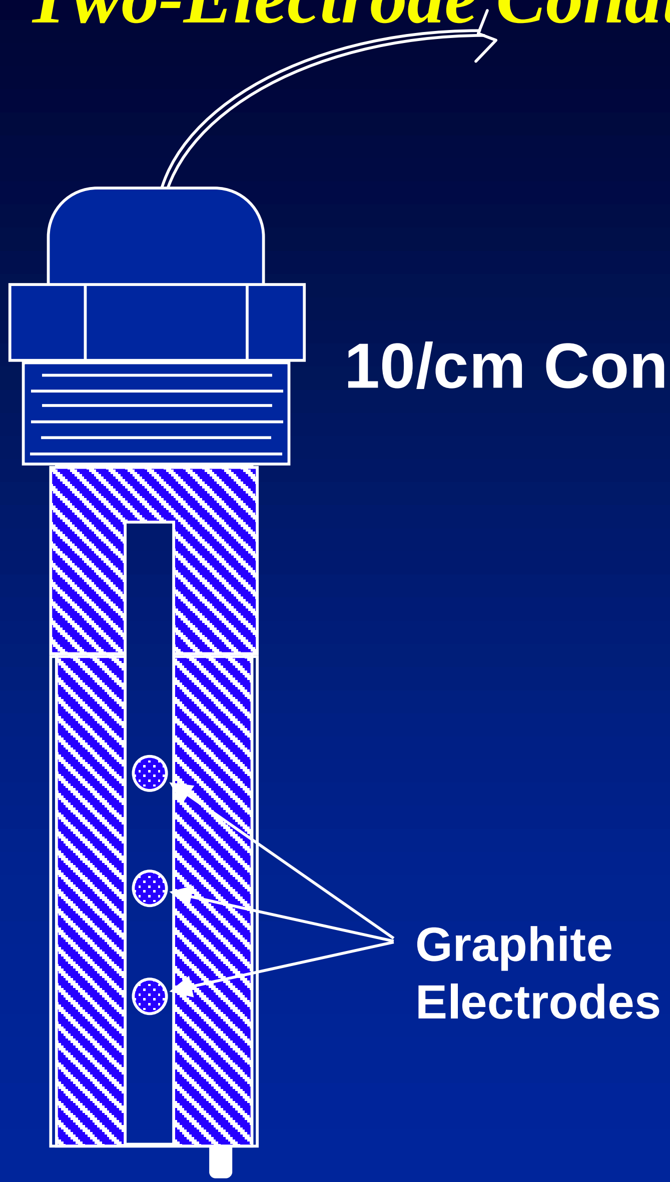


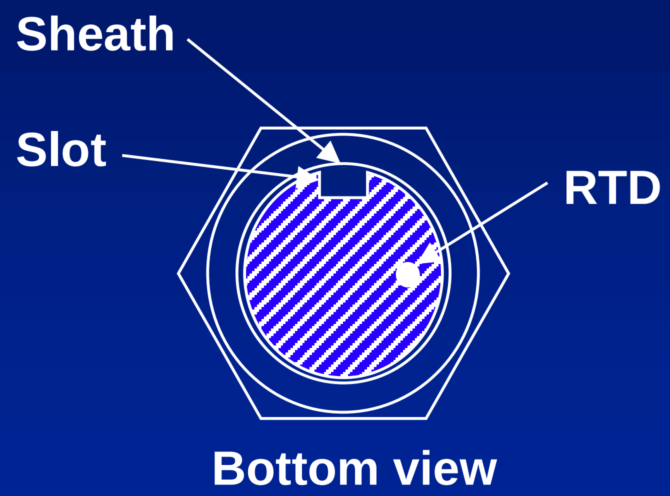
Two-Electrode Conductivity Measurement



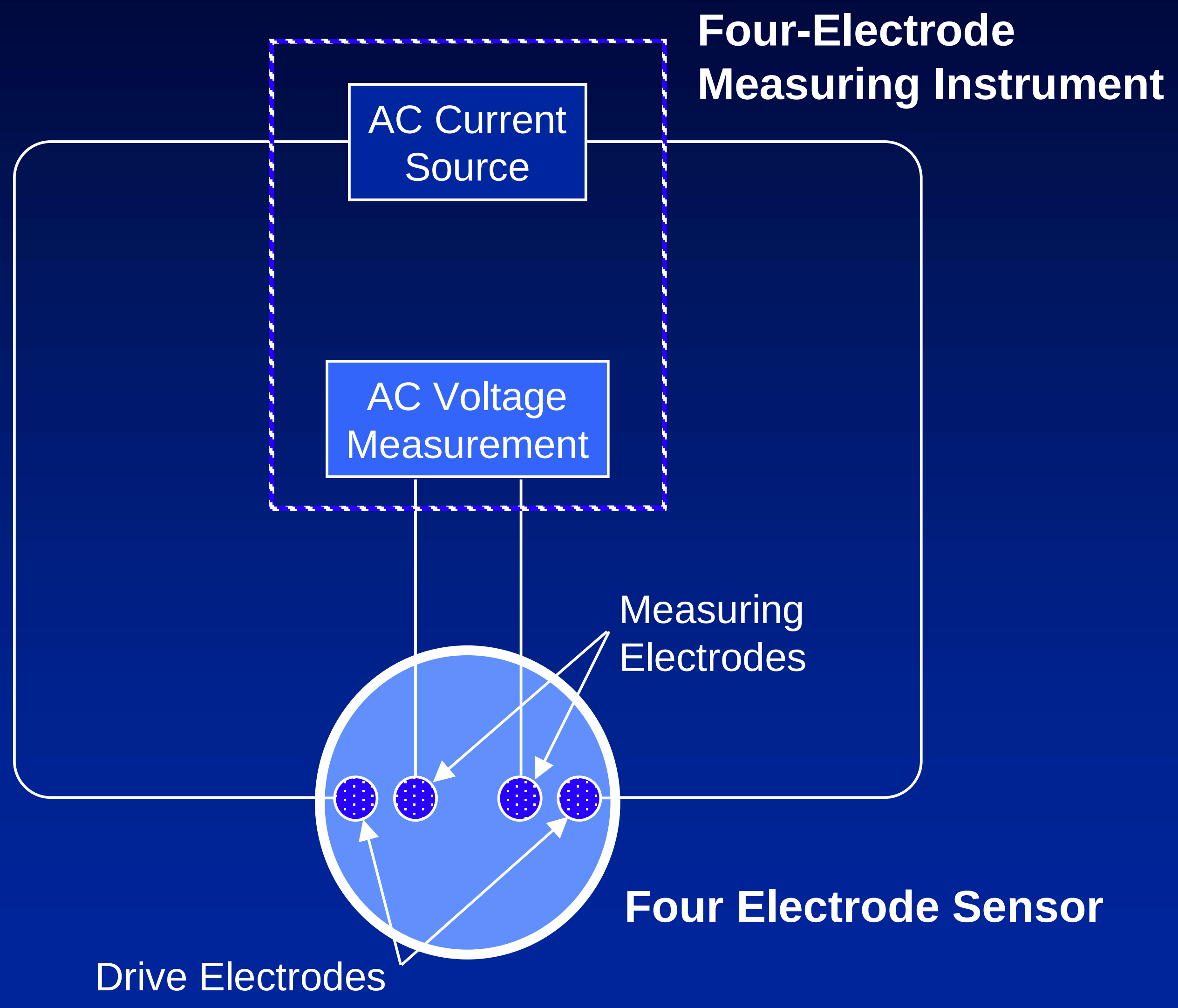


Two-Electrode Conductivity Measurement





Four-Electrode Conductivity Measurement

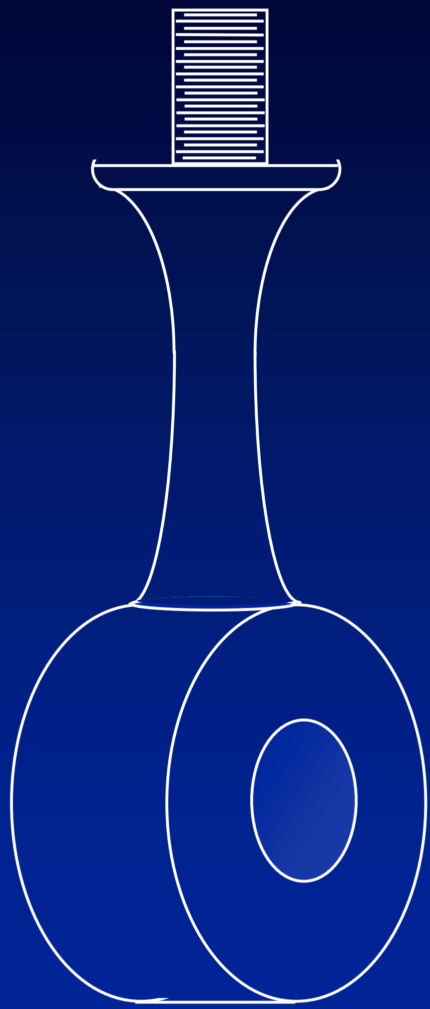


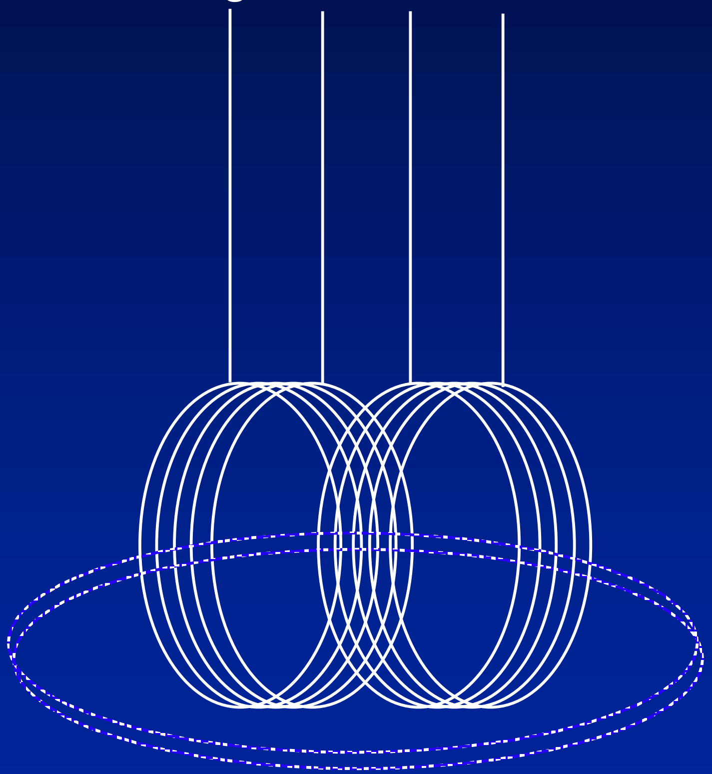
Four-Electrode Conductivity Measurement

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



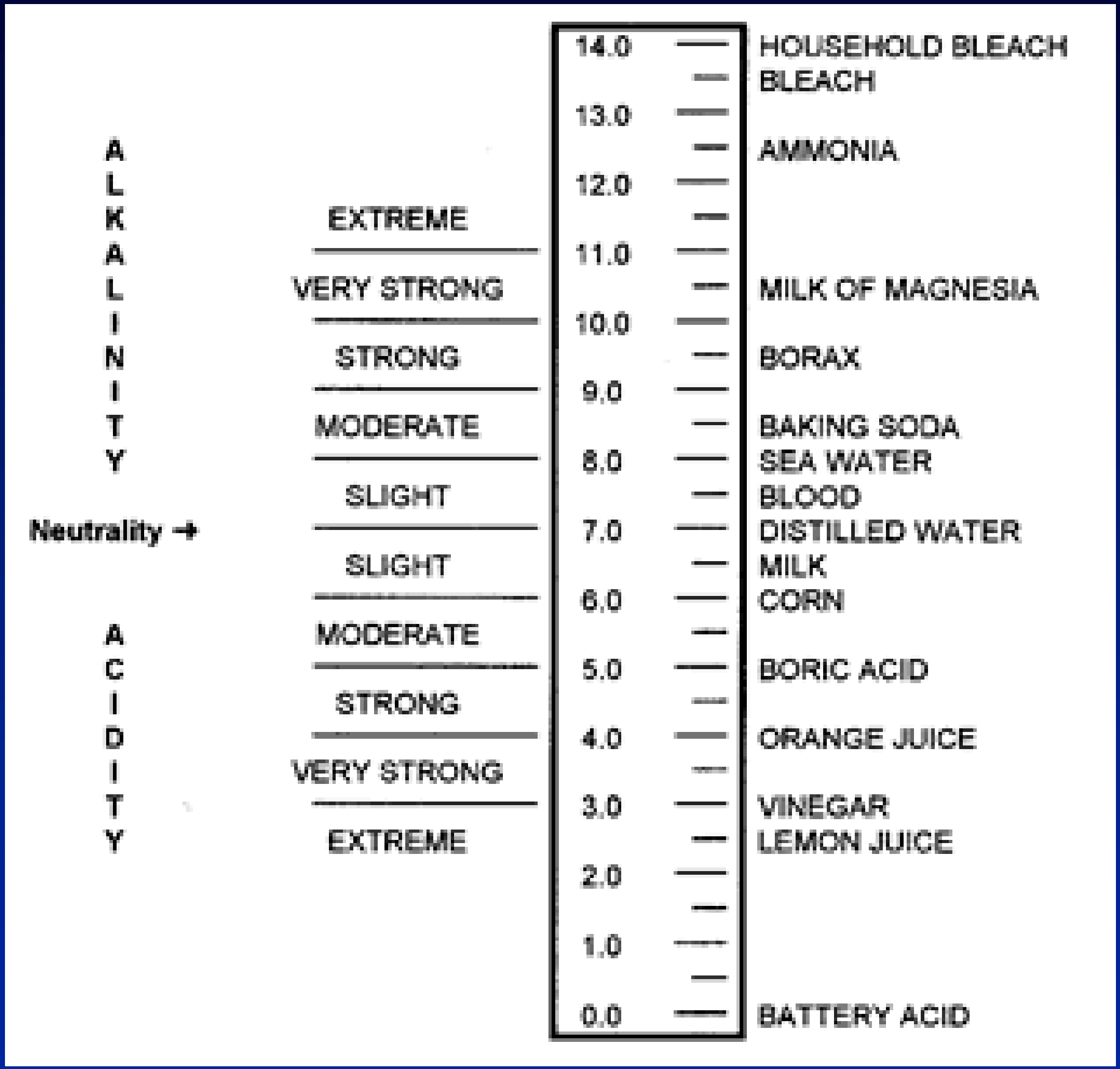


Inductive (non-contact, electrodeless, toroidal) Conductivity Sensor

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



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pH Measurement

Dissociation of water

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w = [H^+]\ [OH^-]$$

pH Scale

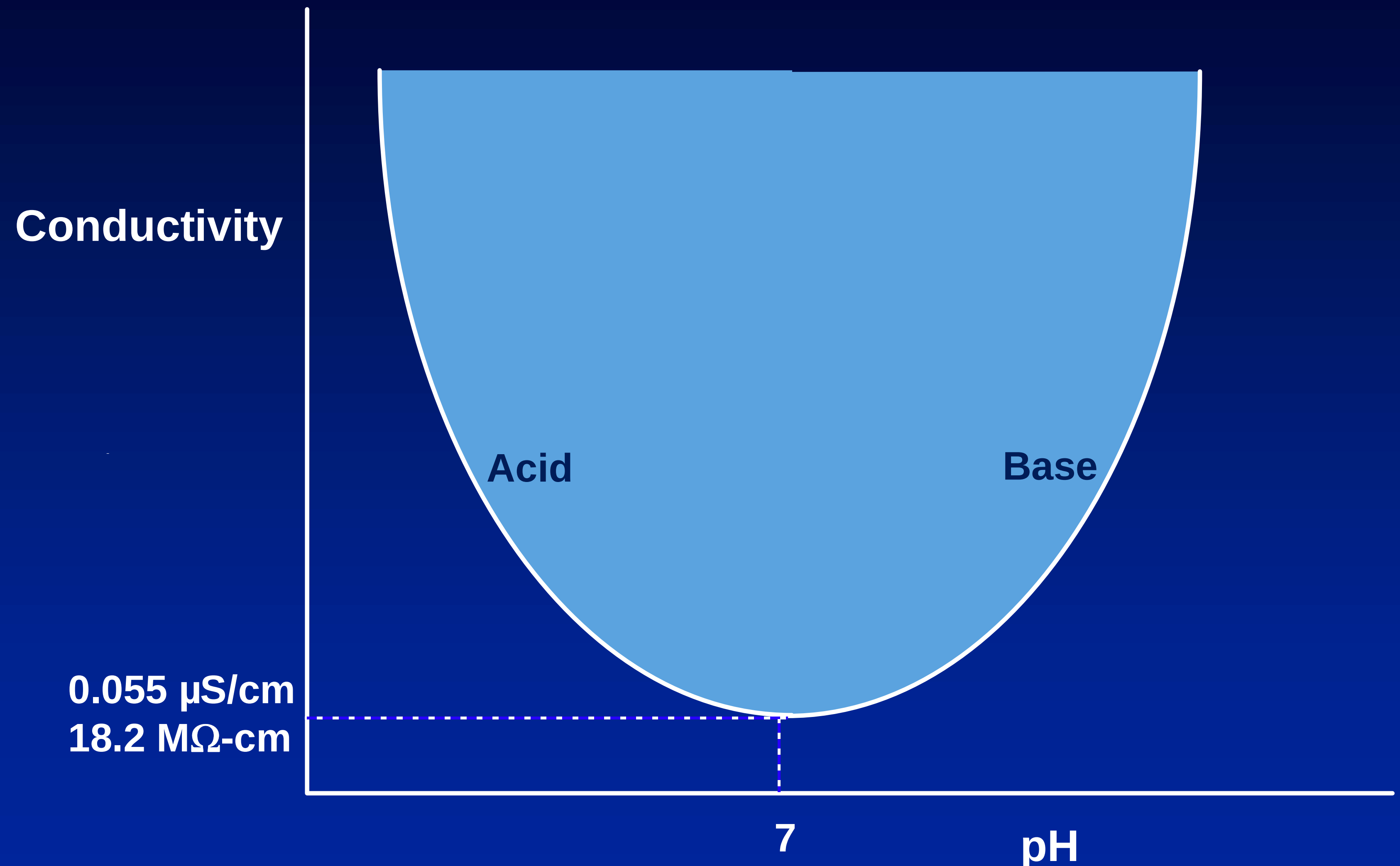
$$pH \sim -\log_{10} [H^+]$$

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

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	pH
10^{-0}	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}	$[H^+]$
10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{-0}	$[OH^+]$

at 25°C

Conductivity vs pH



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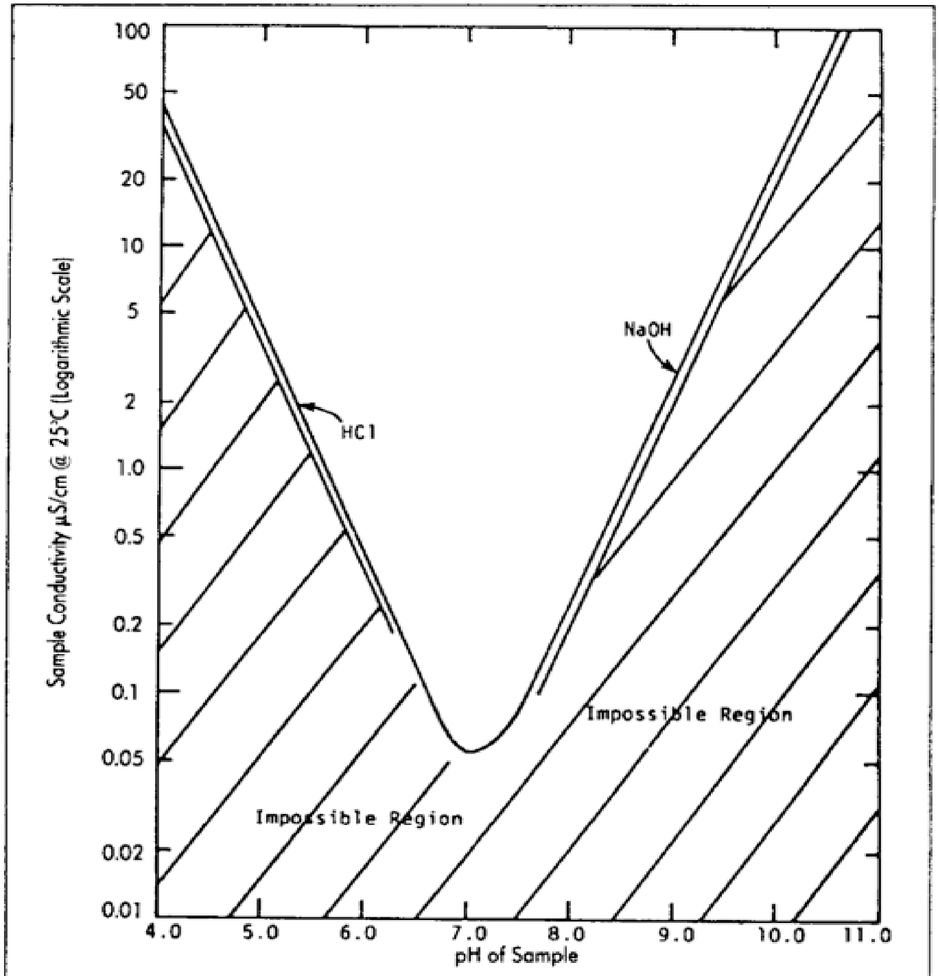
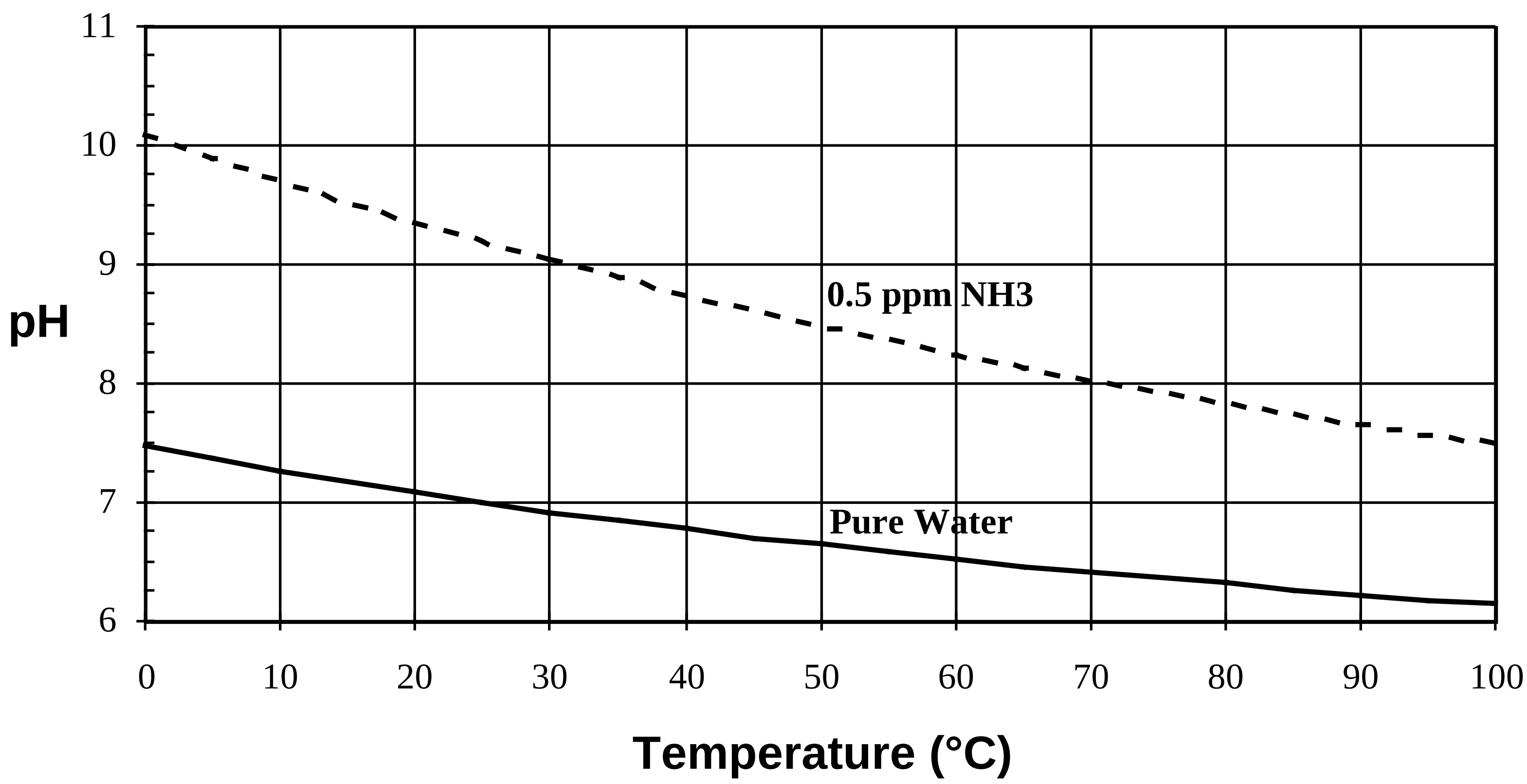
Conductivity vs pH

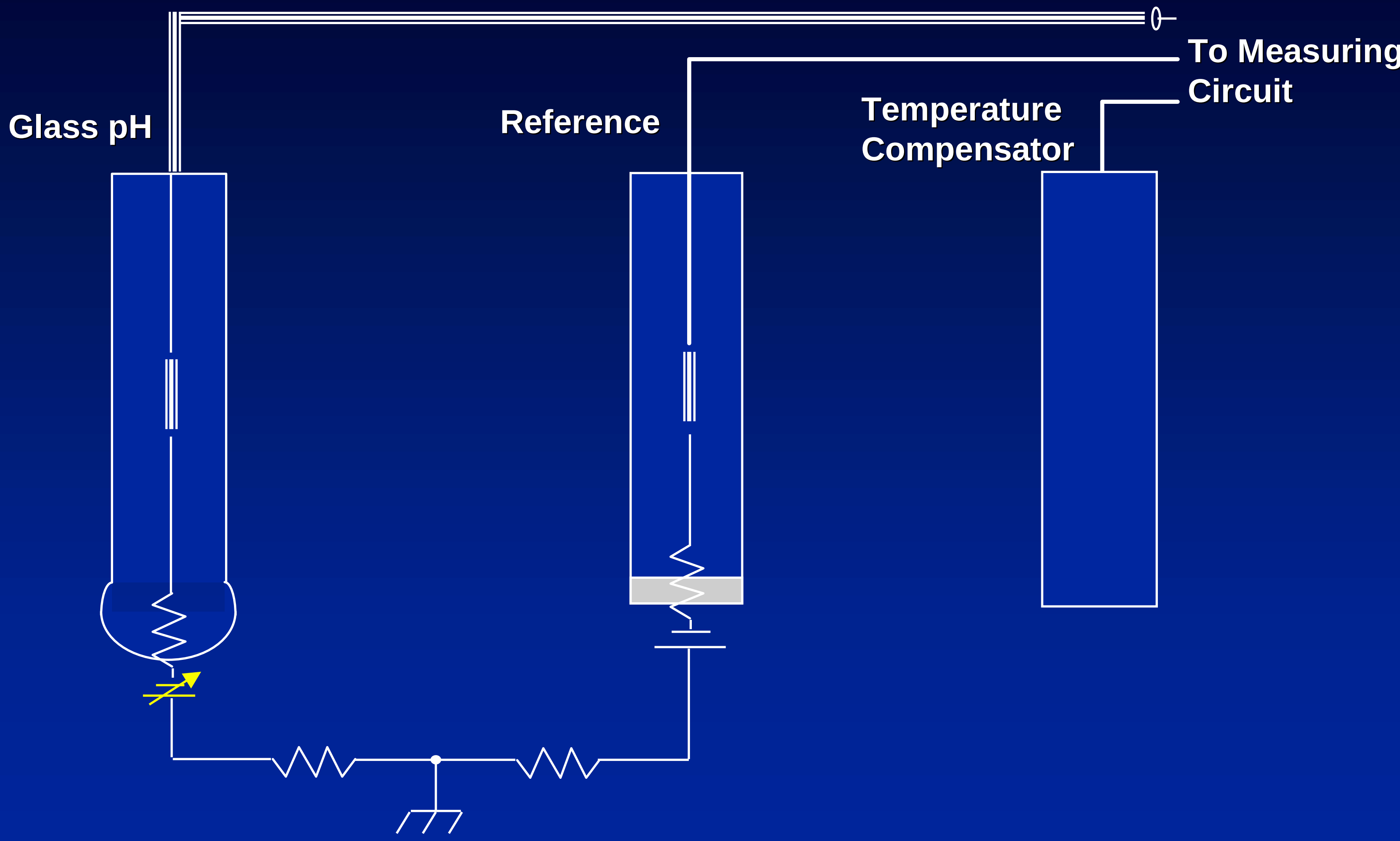


(Courtesy EPRI, NP-35891).

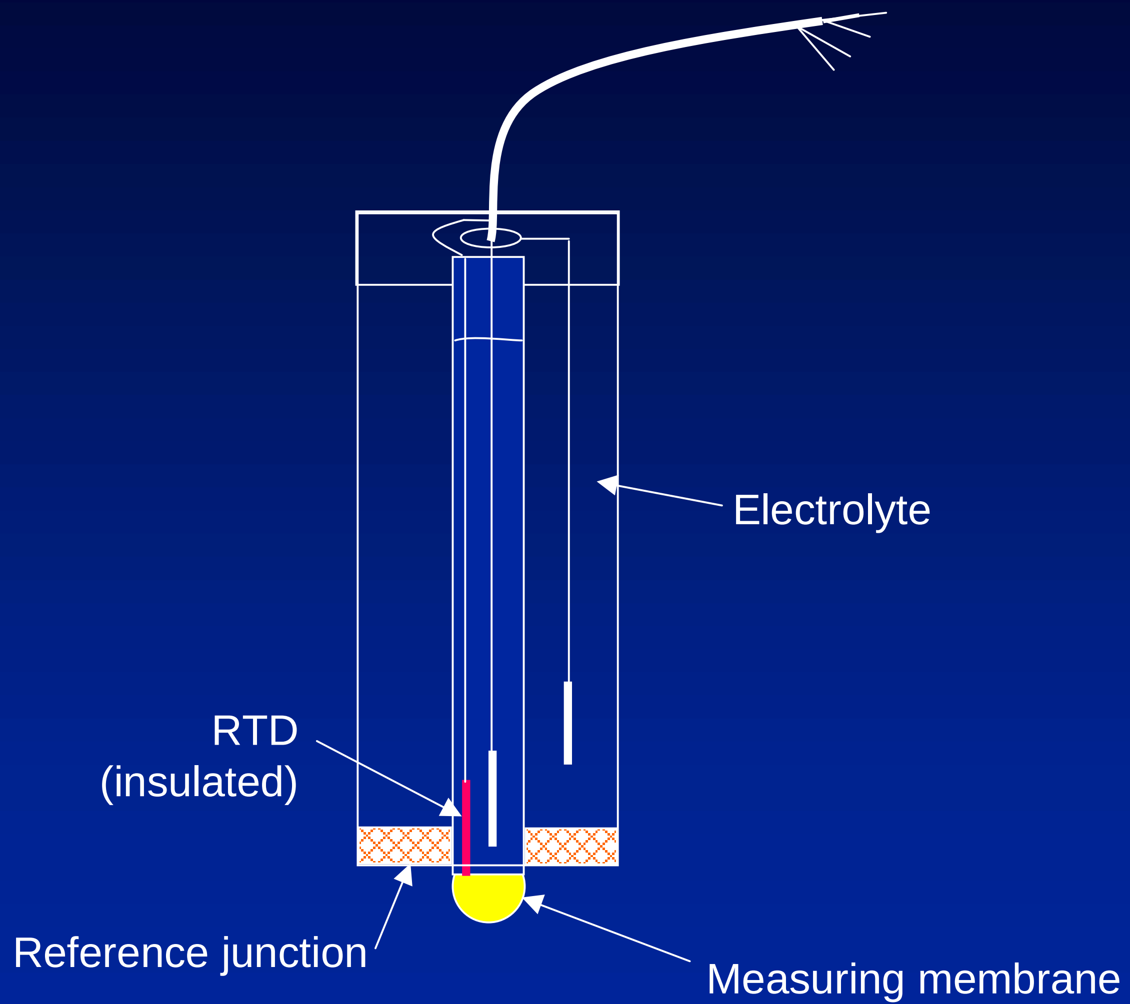
pH vs. Temperature for Pure Waters



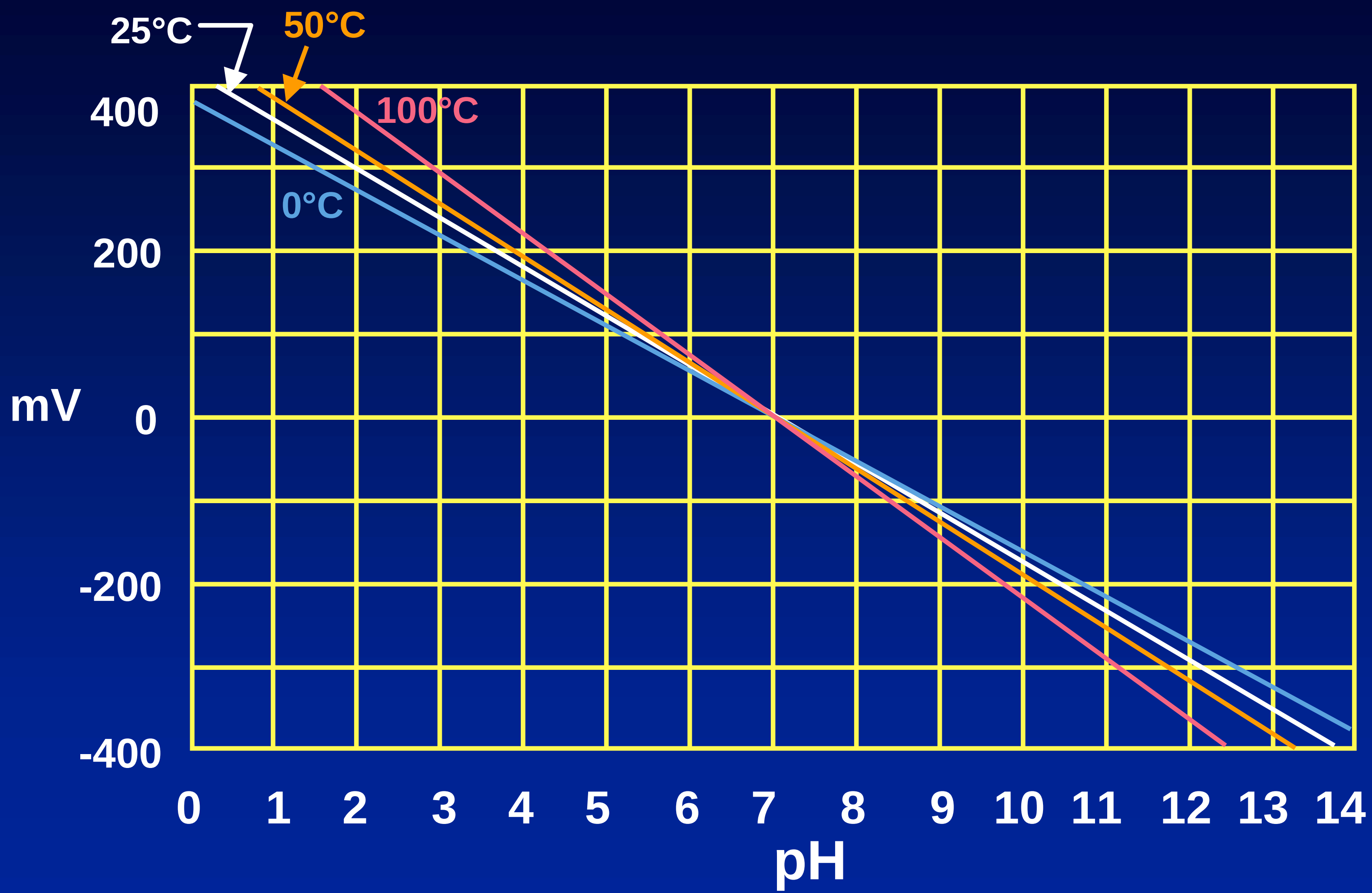
pH Electrode System



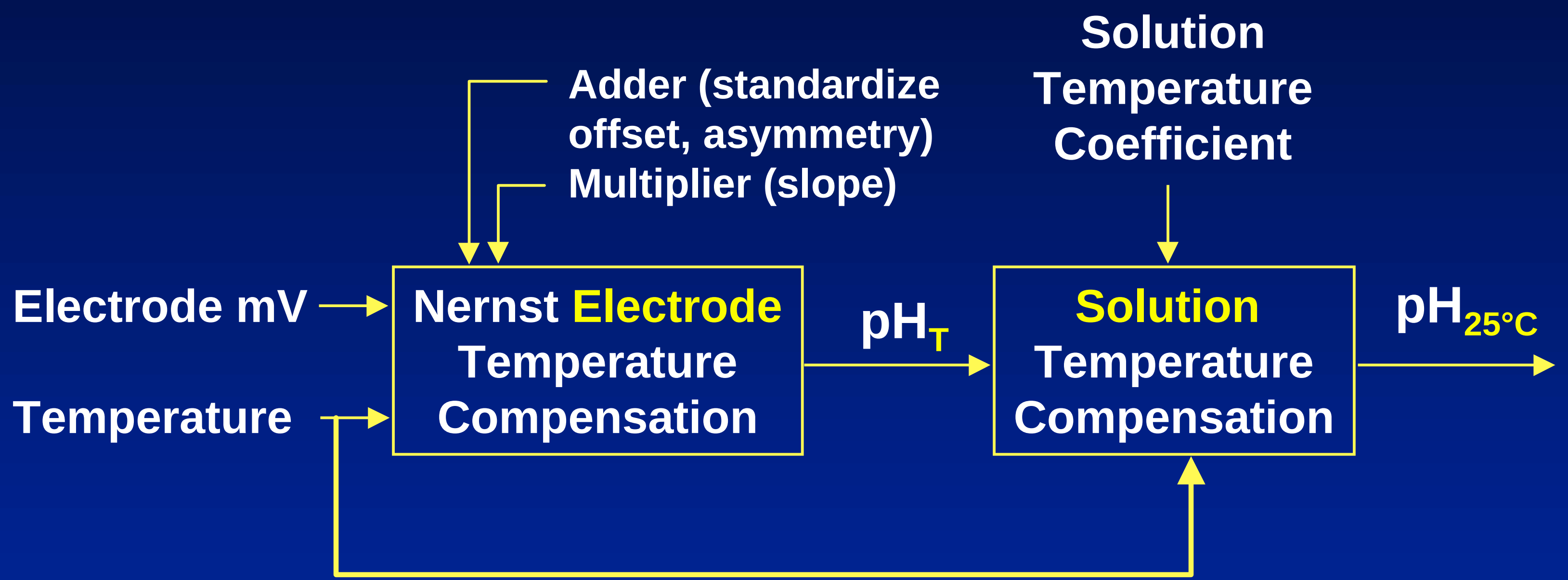
Combination pH Electrode



pH Electrode Output

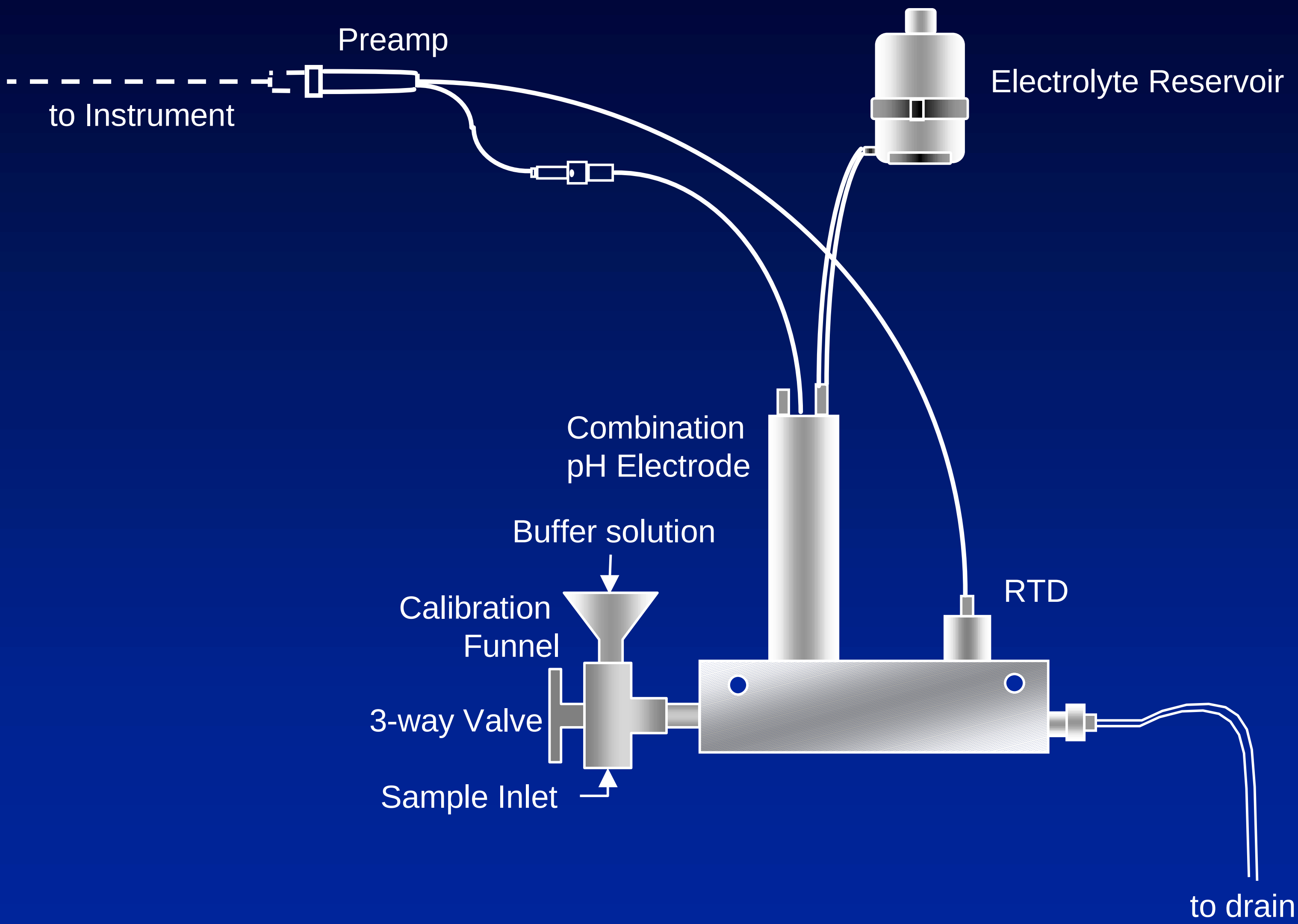


pH Temperature Compensation



Detachable pH Electrode System

High Purity pH Sensor Assembly



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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**

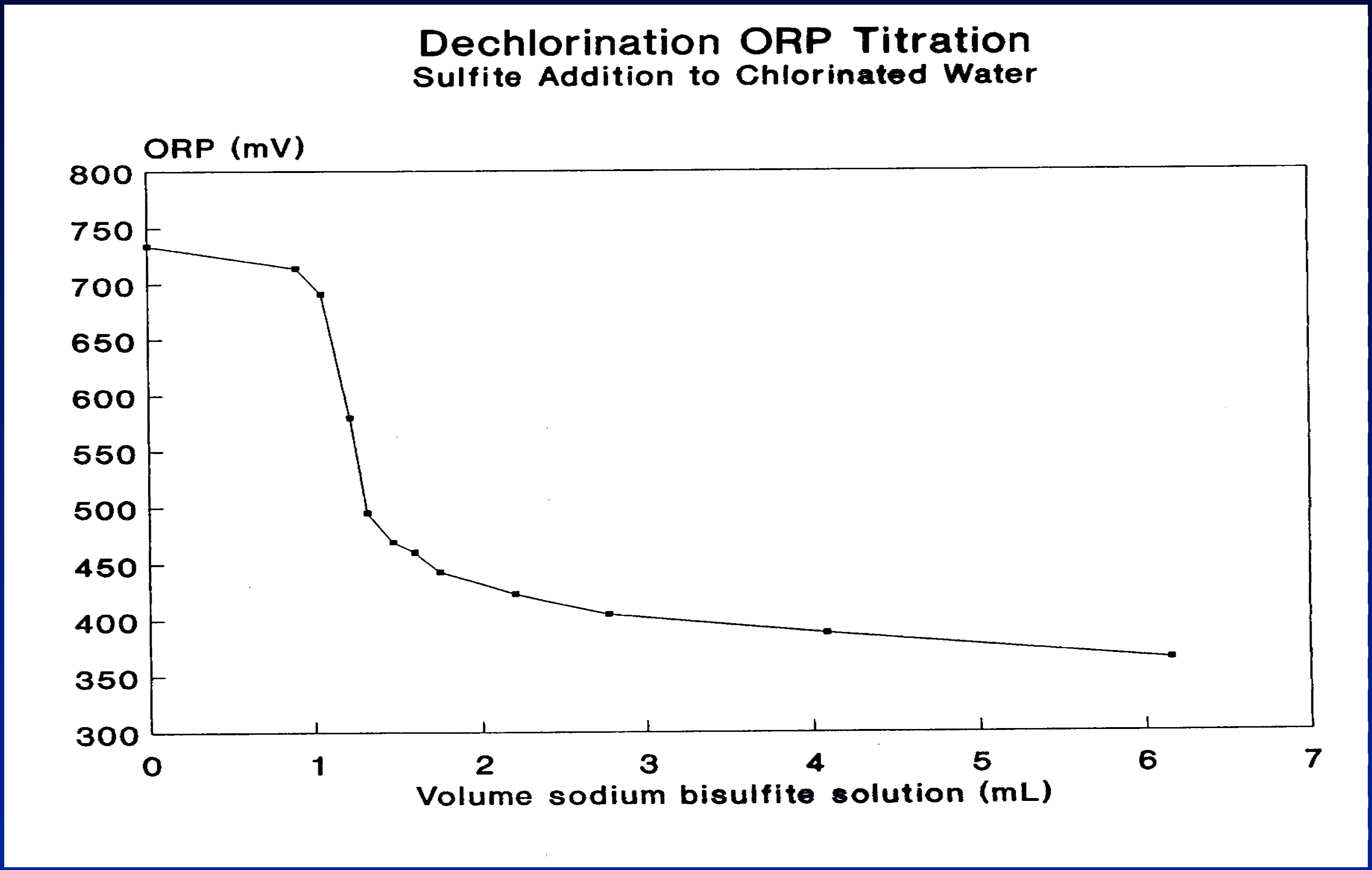
High Purity pH Measurement Equipment

- **Low volume, stainless steel flow chamber**
- **Low sample flowrate with atmospheric discharge**
- **Flowing junction reference electrode**
- ***Solution* temperature compensation as well as *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



ORP Electrode System