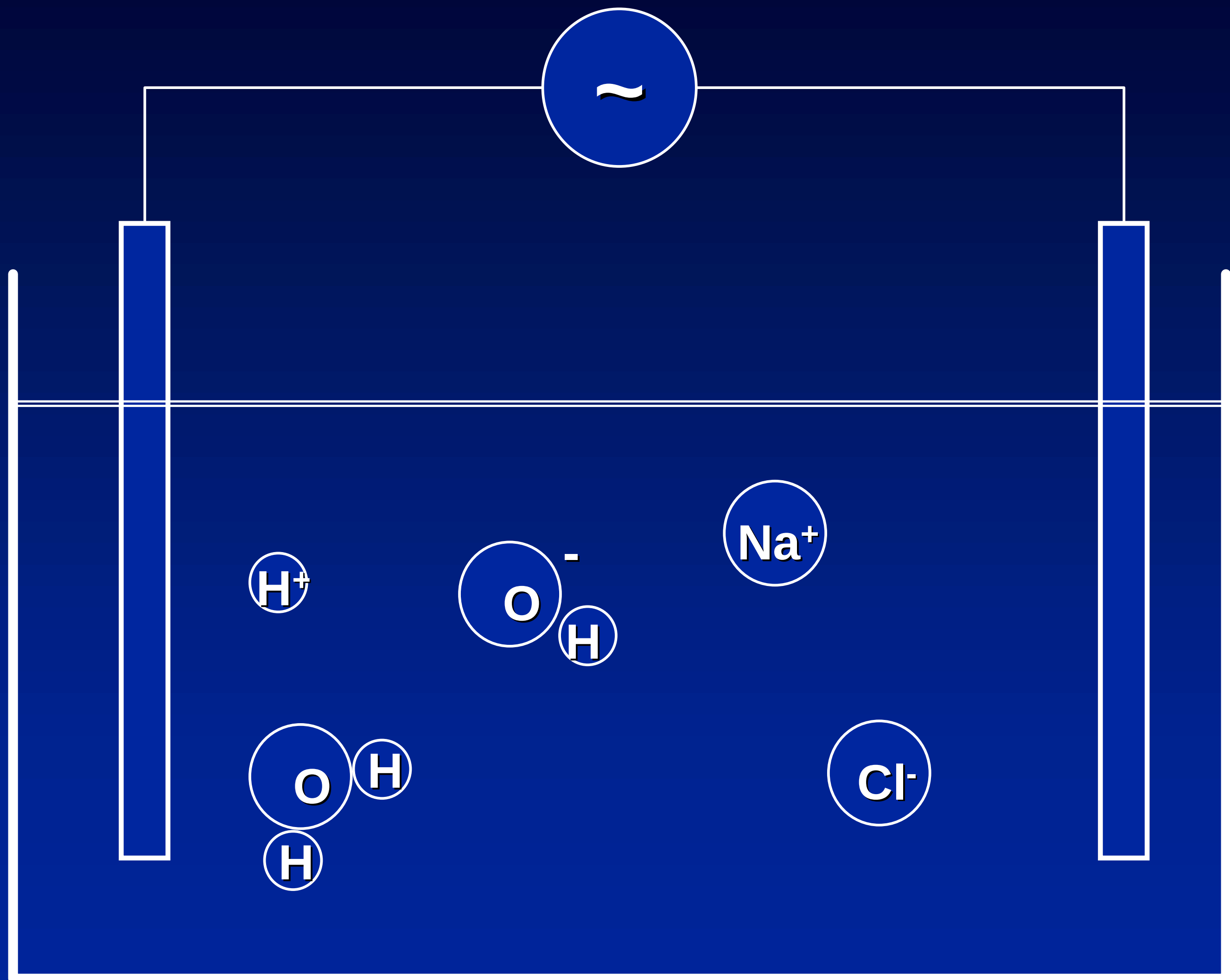
Theory of Liquid Measurements

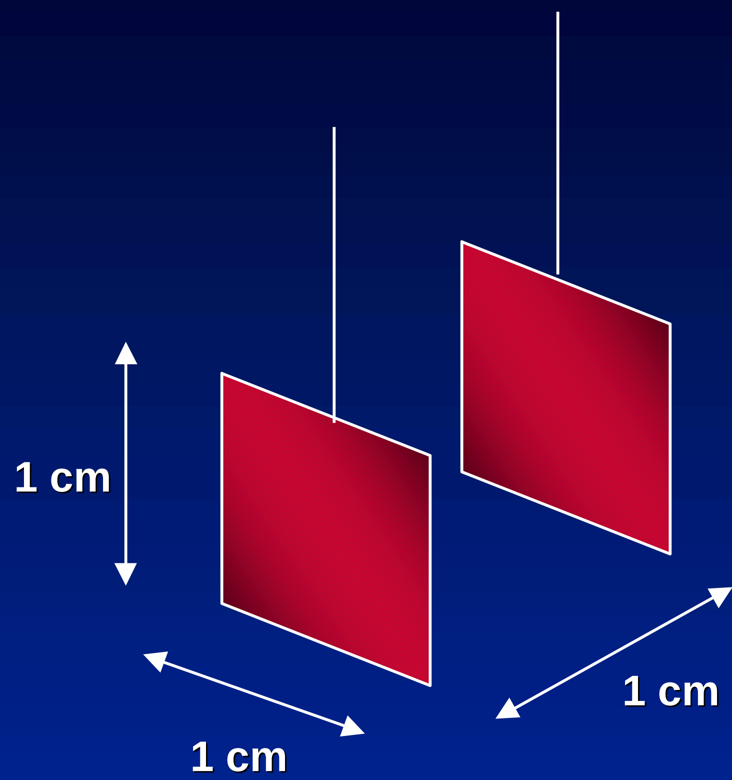
- ***Conductivity/Resistivity***
- ***pH***
- ***ORP***

Ionic Conductance



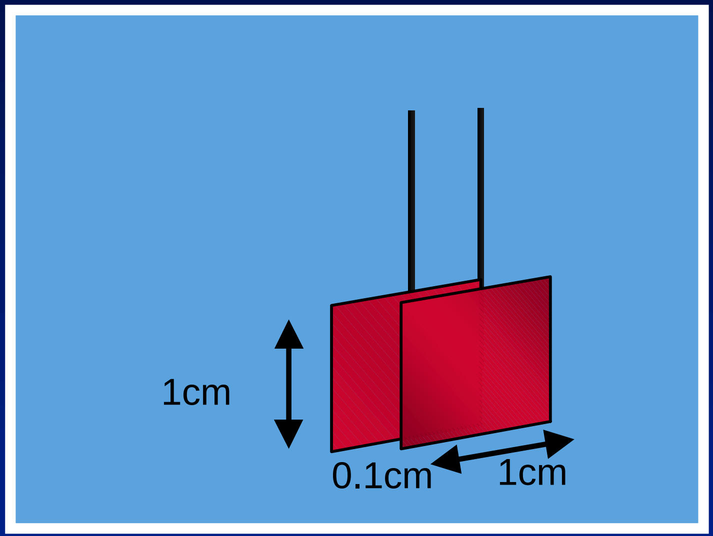
THORNTON / METTLER TOLEDO

Cell Constant

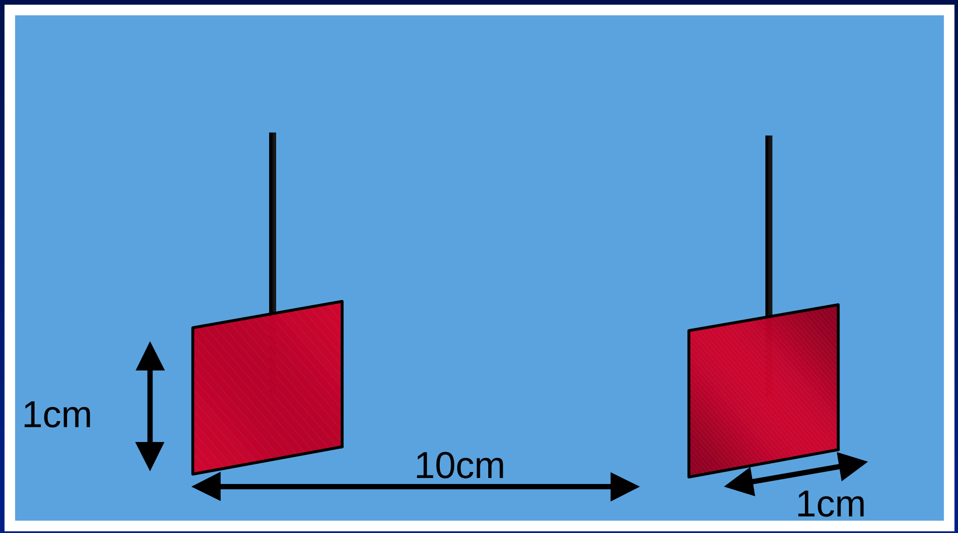


Conductivity Cell Constant $= \dfrac{\text{Length}}{\text{Area}} = \dfrac{1\ \text{cm}}{1\ \text{cm}^2} = 1\ \text{cm}^{-1}$

Other Cell Constants



0.1 constant

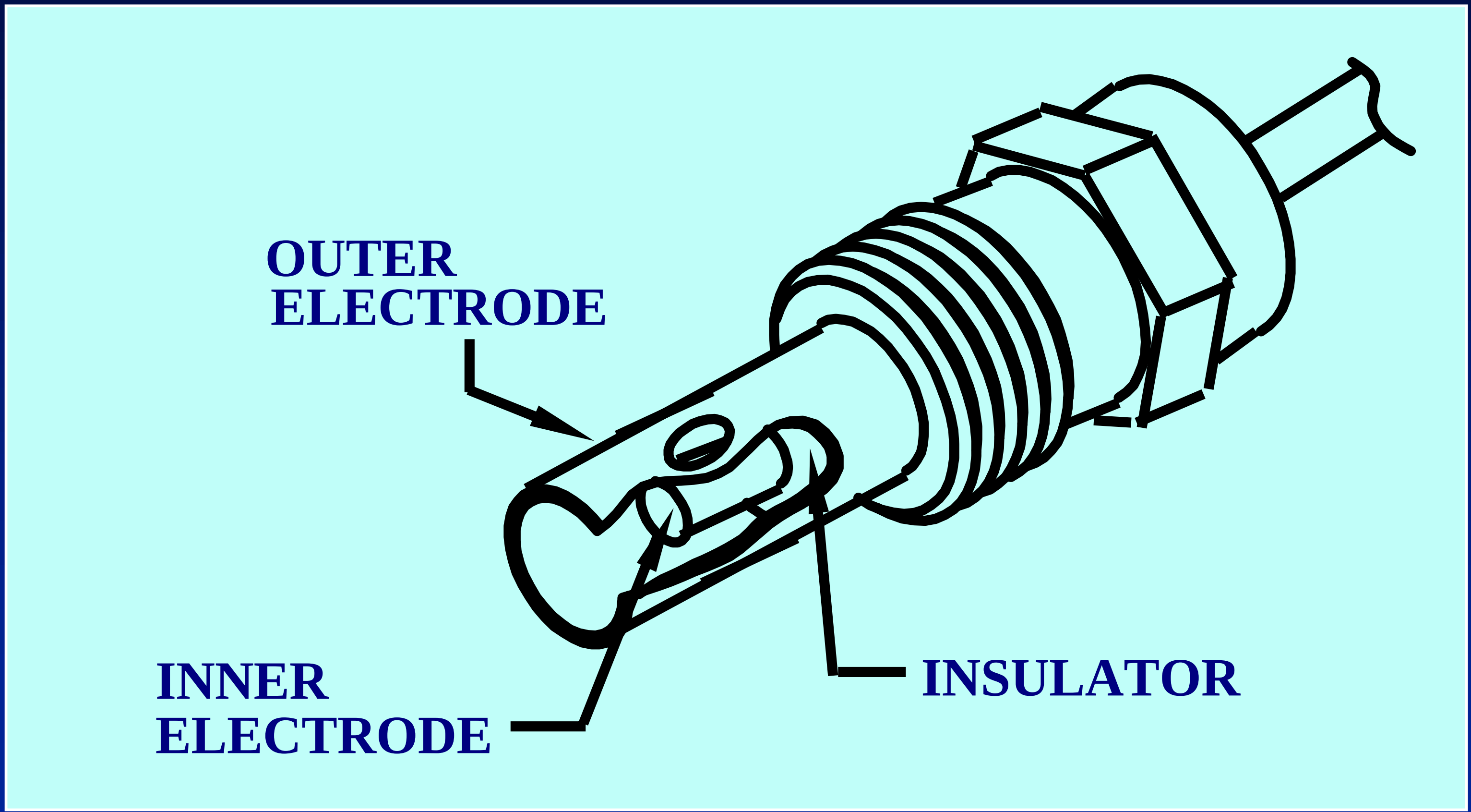


10.0 constant

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)

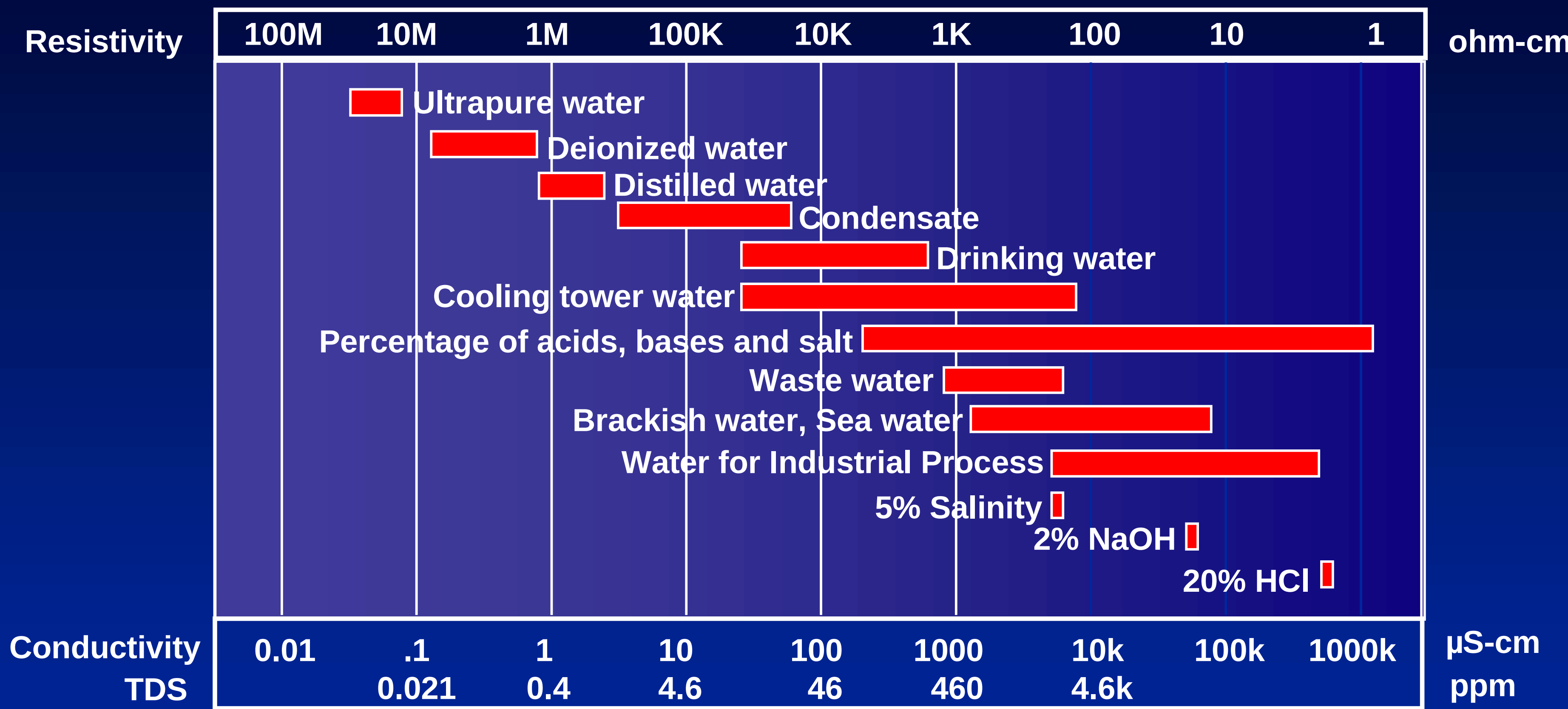
Cell Constant Traceability

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.

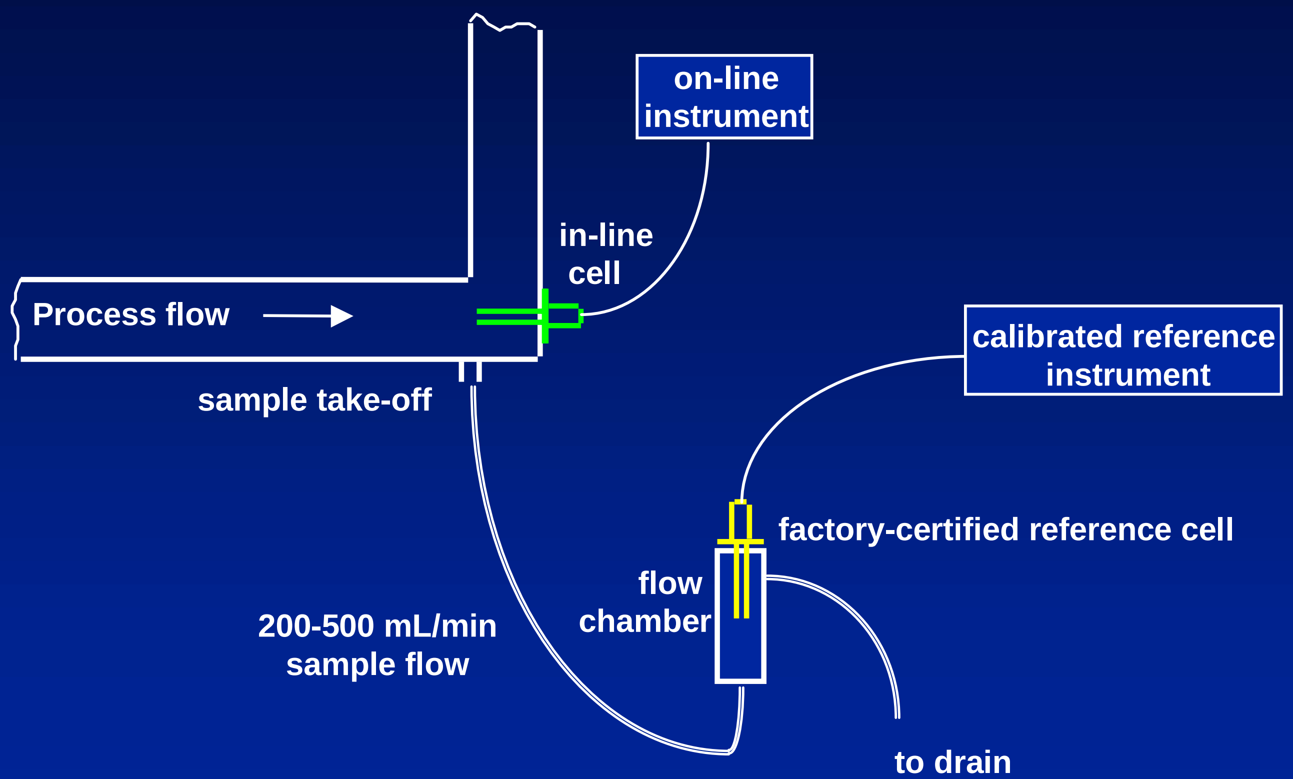
Conductivity, Resistivity, TDS Ranges



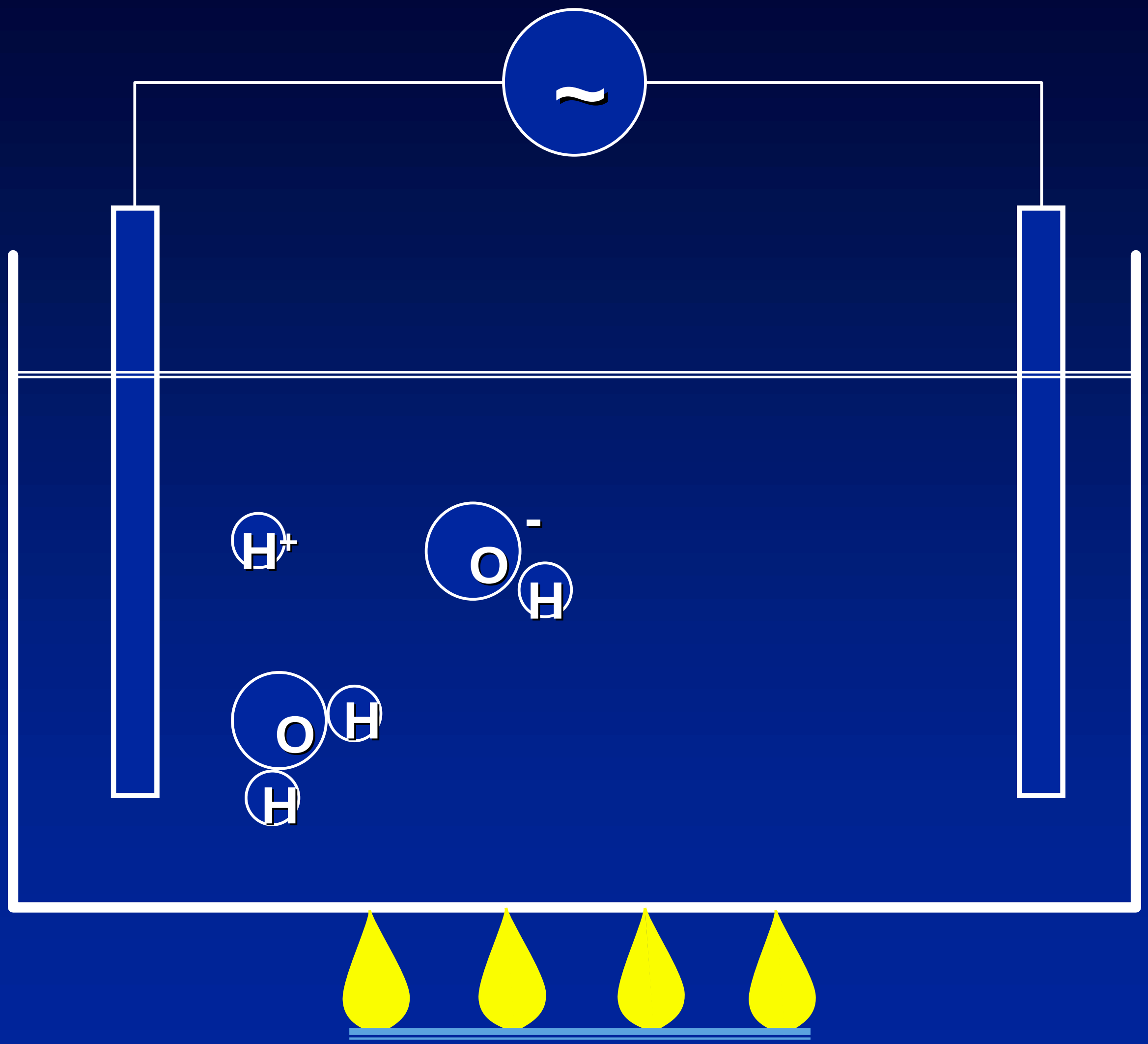
Conductivity and resistivity are measured at 25°C; TDS is expressed as Sodium Chloride (NaCl)

THORNTON / METTLER TOLEDO

On-Line Conductivity Sensor Calibration/Verification



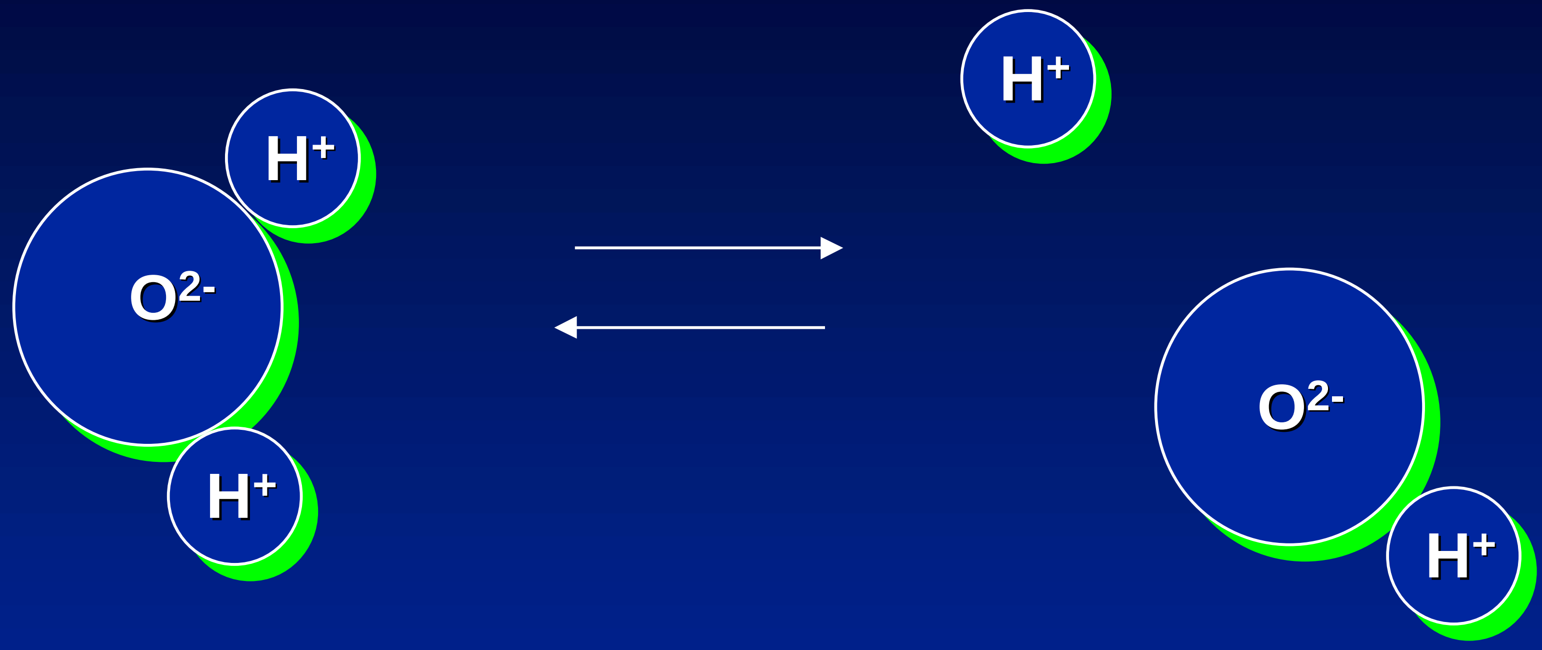
Temperature Effects on Conductivity



Conductivity/Resistivity Temperature Coefficients

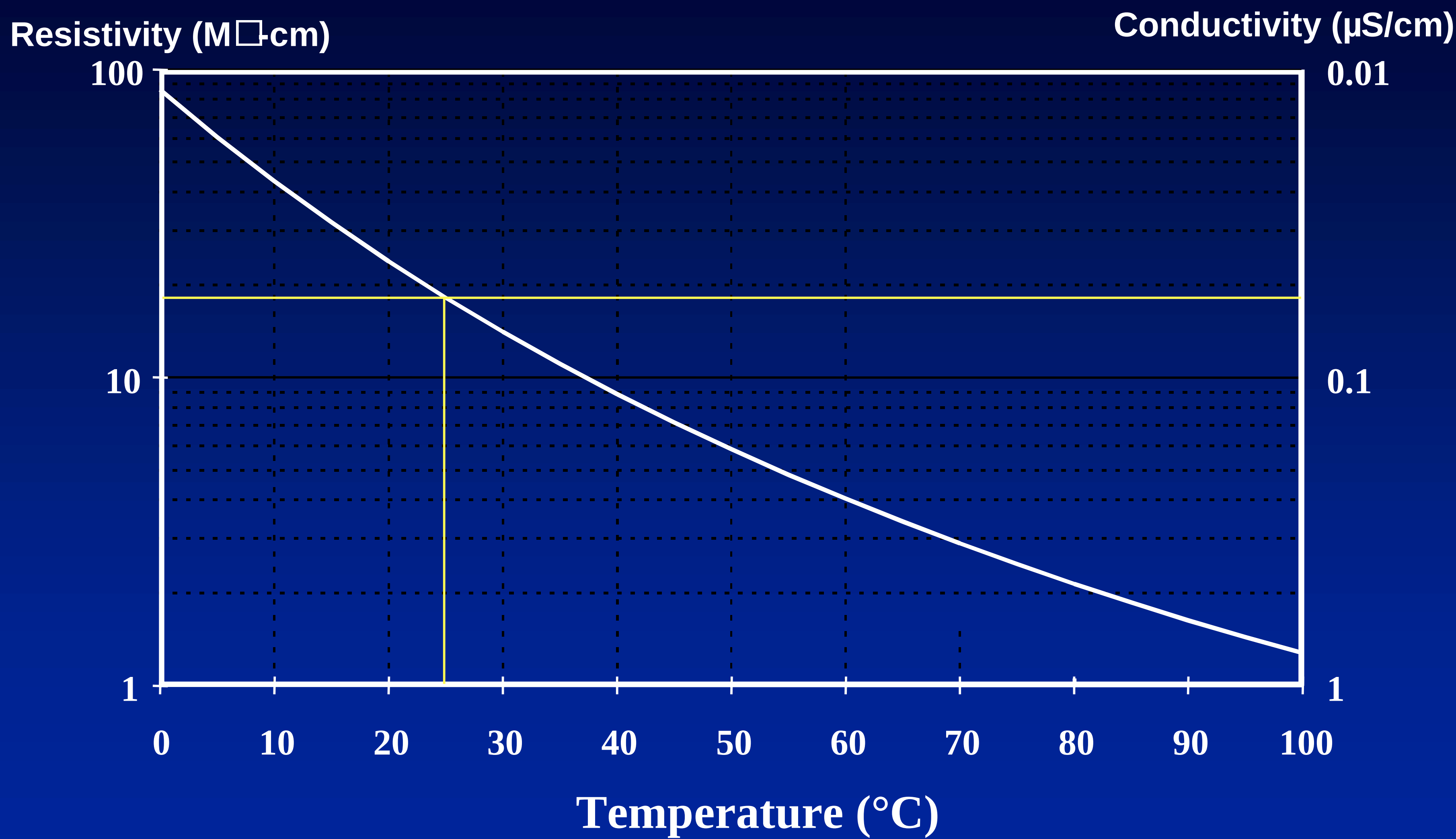
Natural waters, etc. (>2 μS/cm)	**~ 2 %/°C**
High purity water (0.055 μS/cm or 18.2 Megohm-cm)	**4 - 7 %/°C**

Dissociation of Water



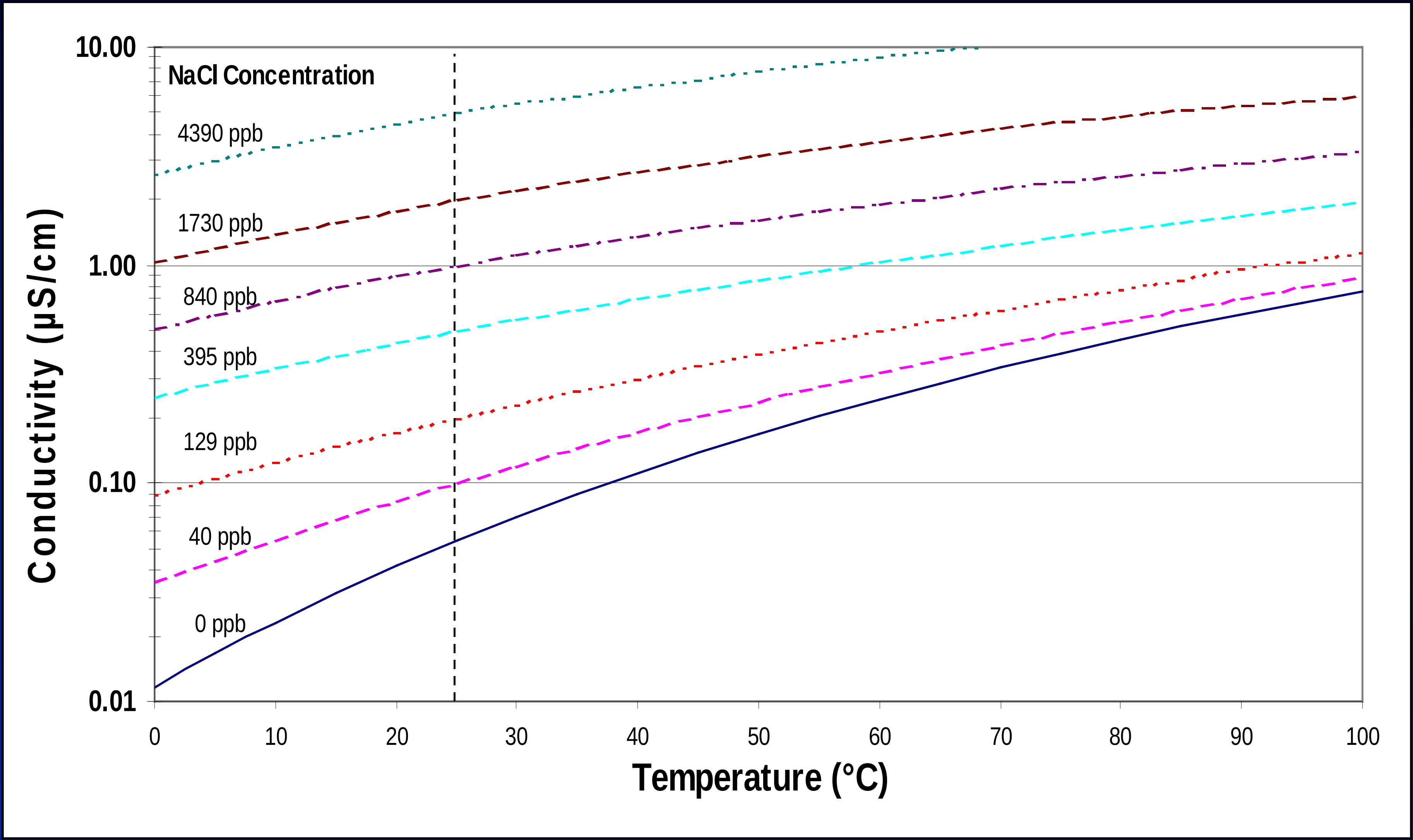
$$H_2O \rightleftharpoons H^+ + OH^-$$

Conductivity of Pure Water vs. Temperature



THORNTON / METTLER TOLEDO

Conductivity vs. Temperature

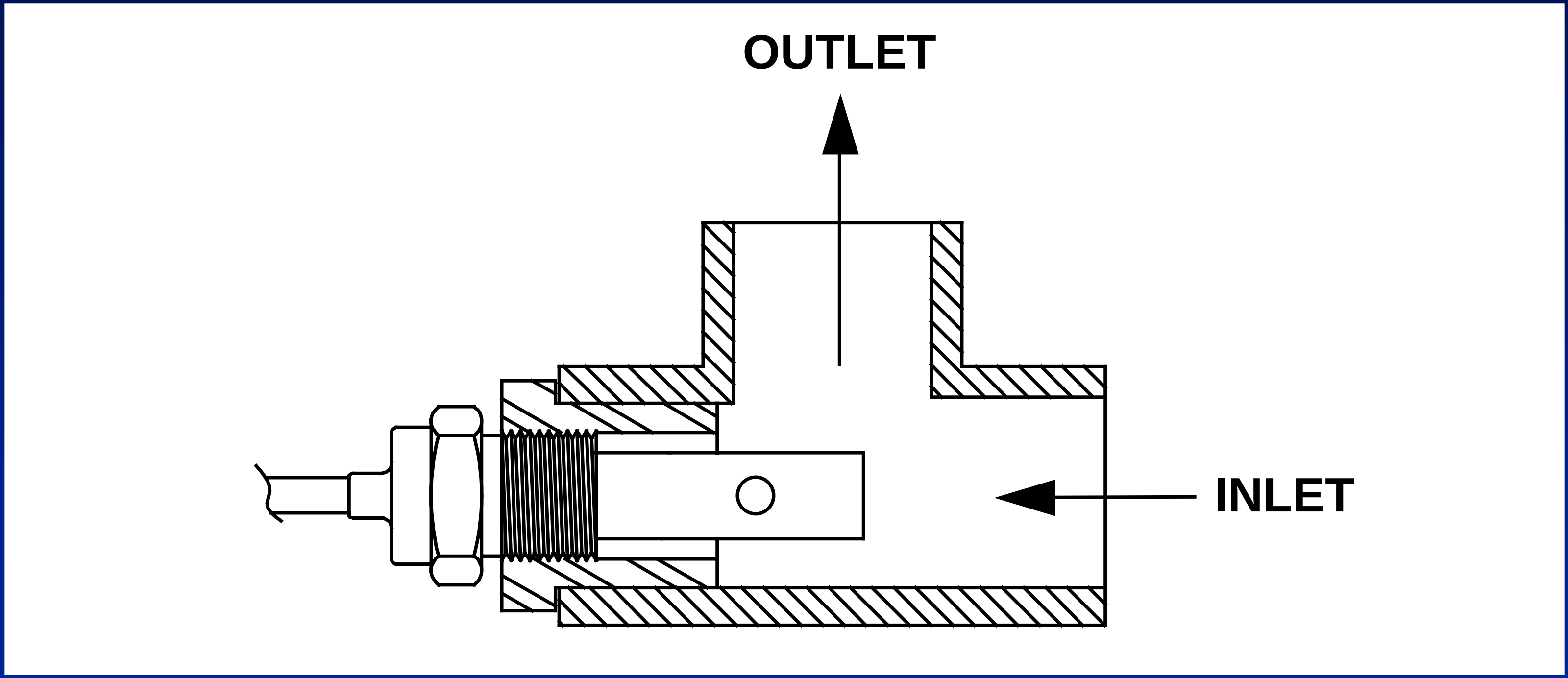


Temperature Compensation

- **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...



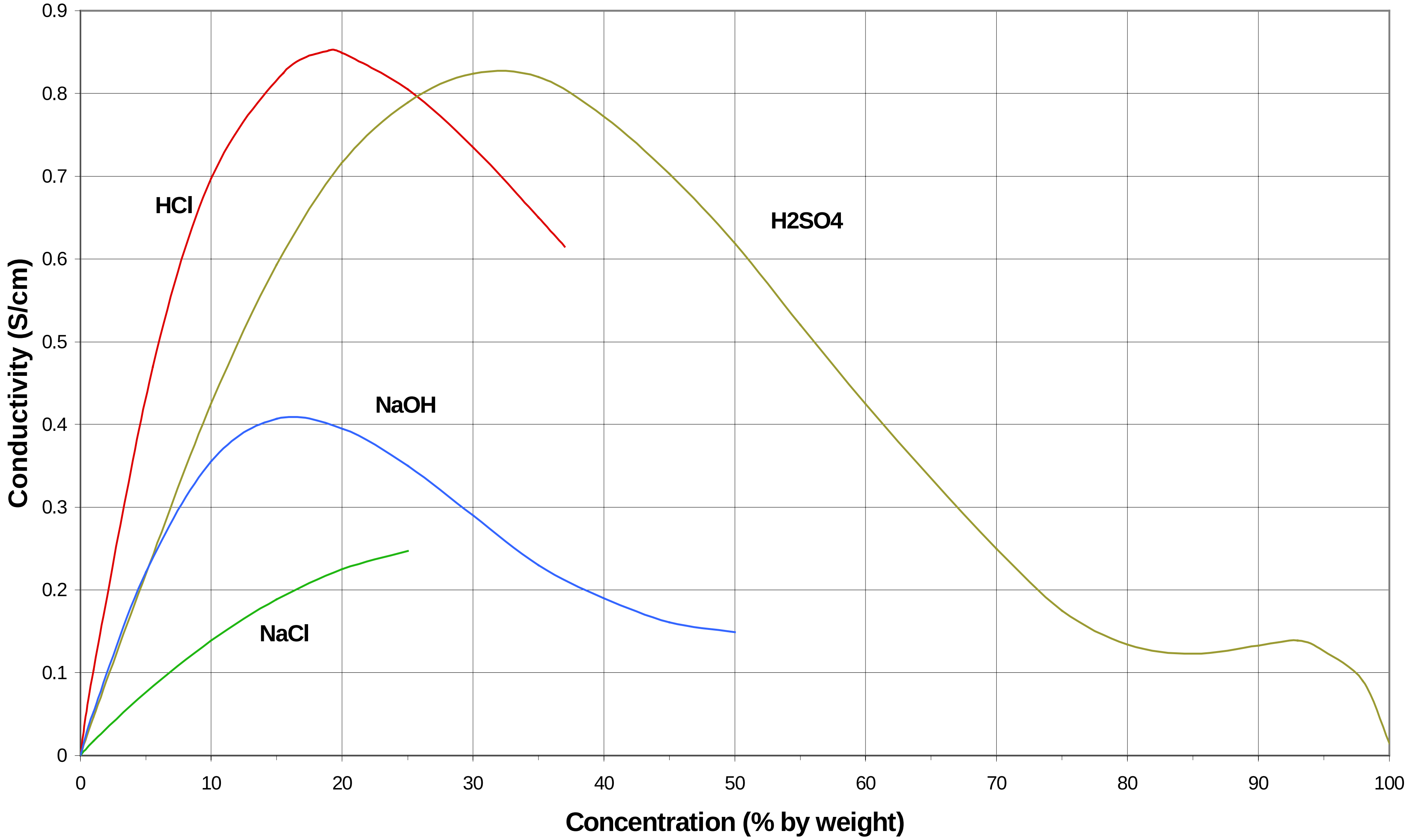
Flow should be directed at the end of the sensor

High Conductivity Measurements

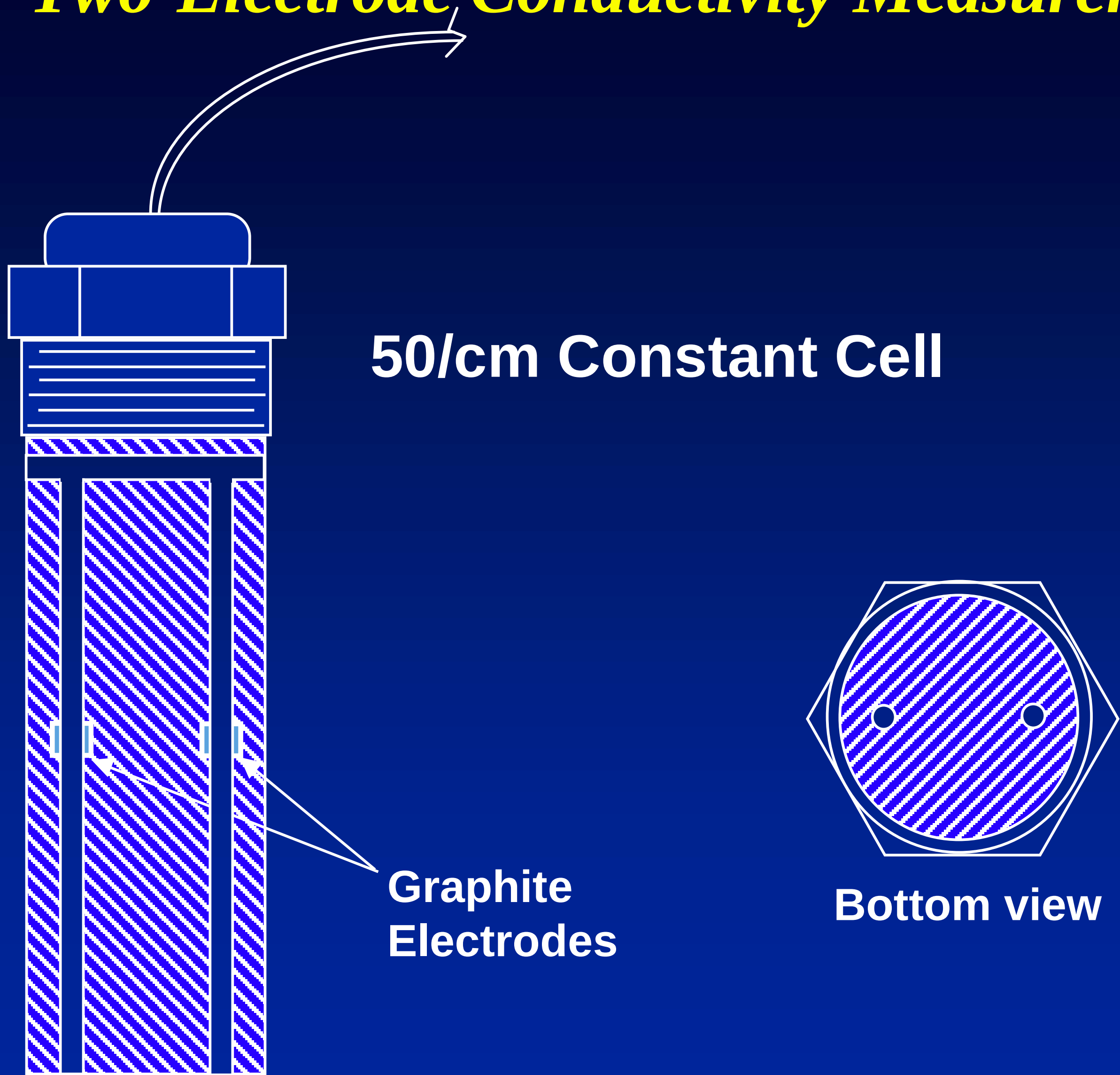
- **Applications**
  - **Reverse Osmosis feedwater**
  - **Acid/Base deionizer regenerant concentration**
  - **Process fluids**
  - **Recycle water**
  - **Wastewater/effluent**
  - **Cooling towers**

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

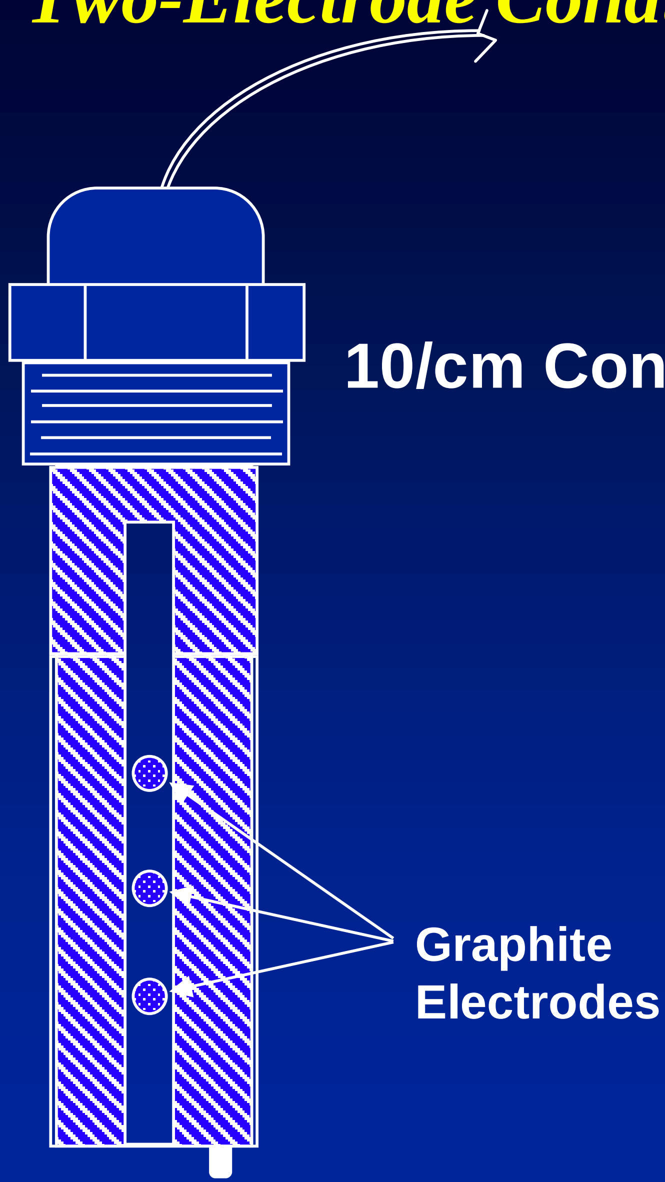
Conductivity vs. Concentration

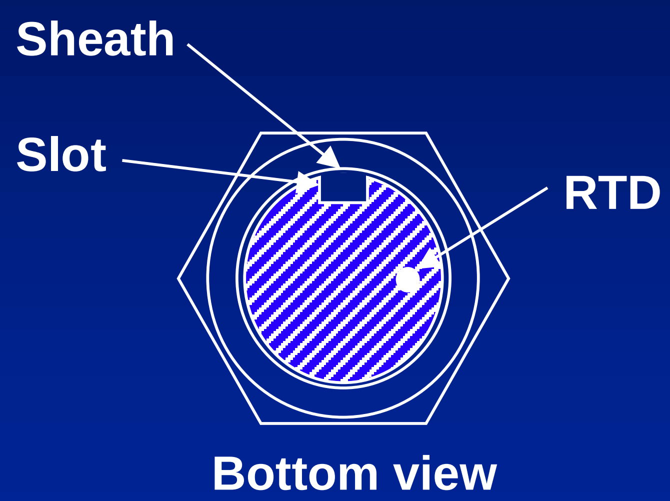


Two-Electrode Conductivity Measurement

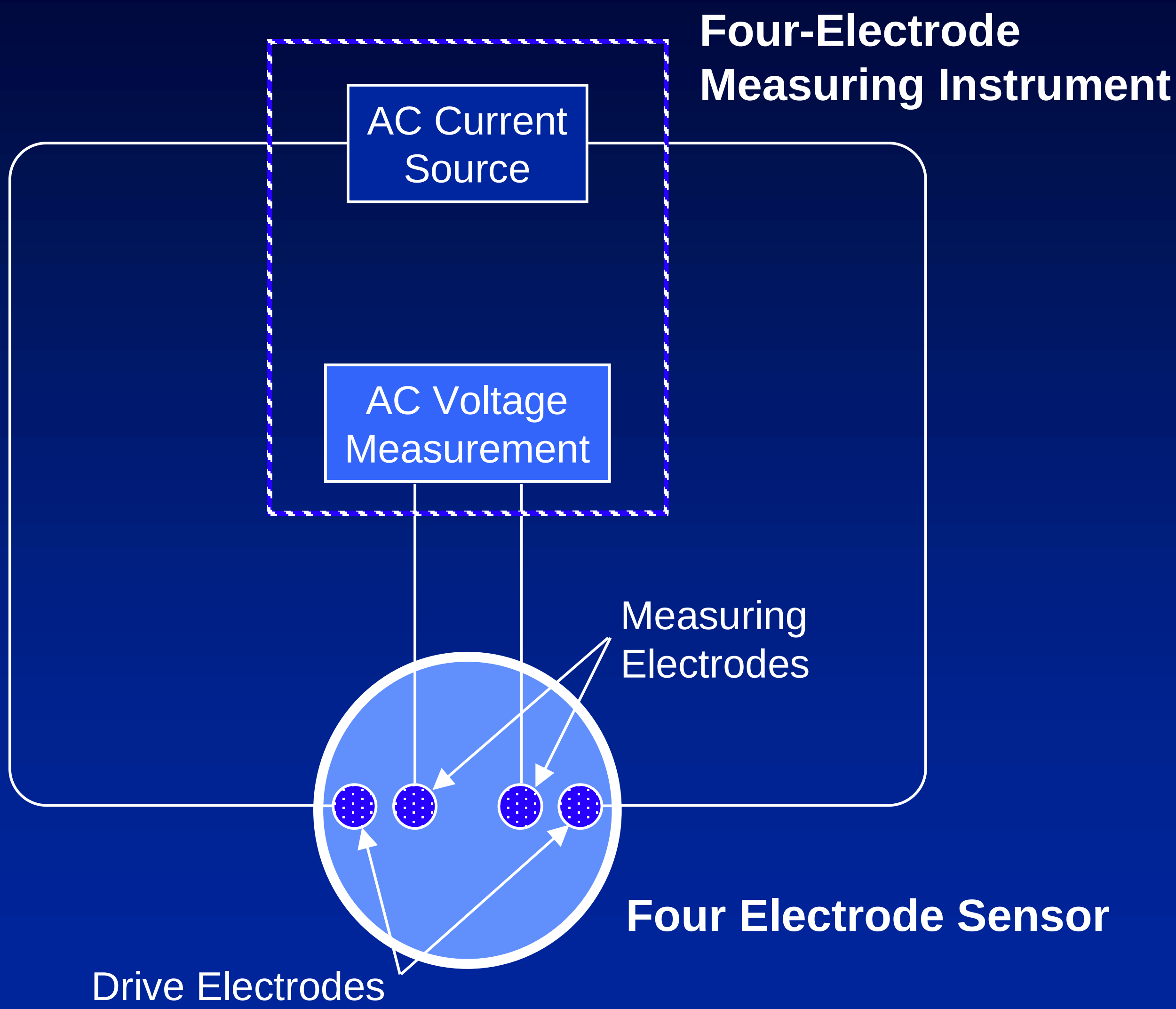


Two-Electrode Conductivity Measurement





Four-Electrode Conductivity Measurement



Four-Electrode Conductivity Measurement

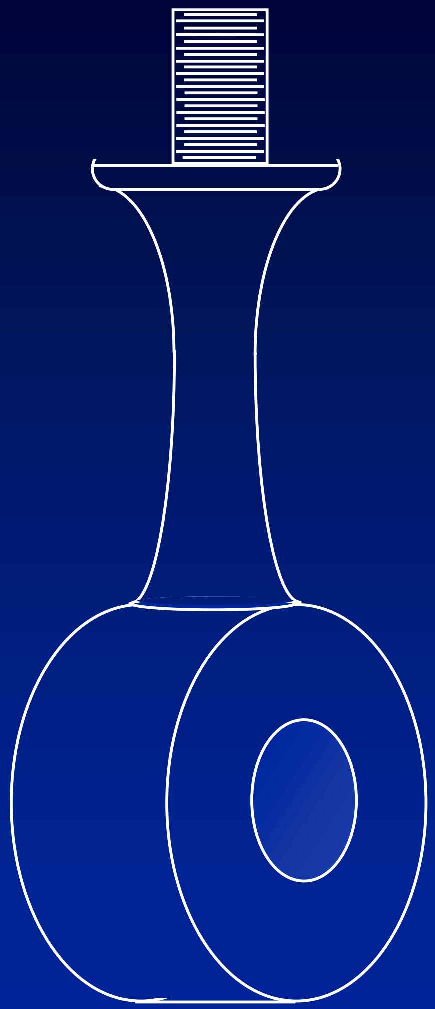
Four-electrode sensors and instruments can tolerate poor measuring conditions due to three factors:

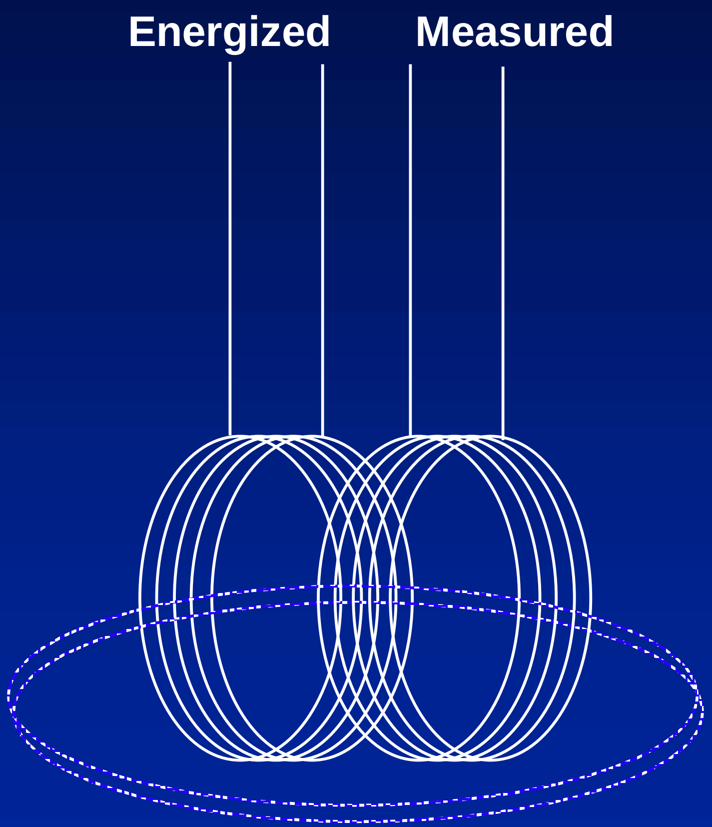
1. Electrode metal surface condition is less important.

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





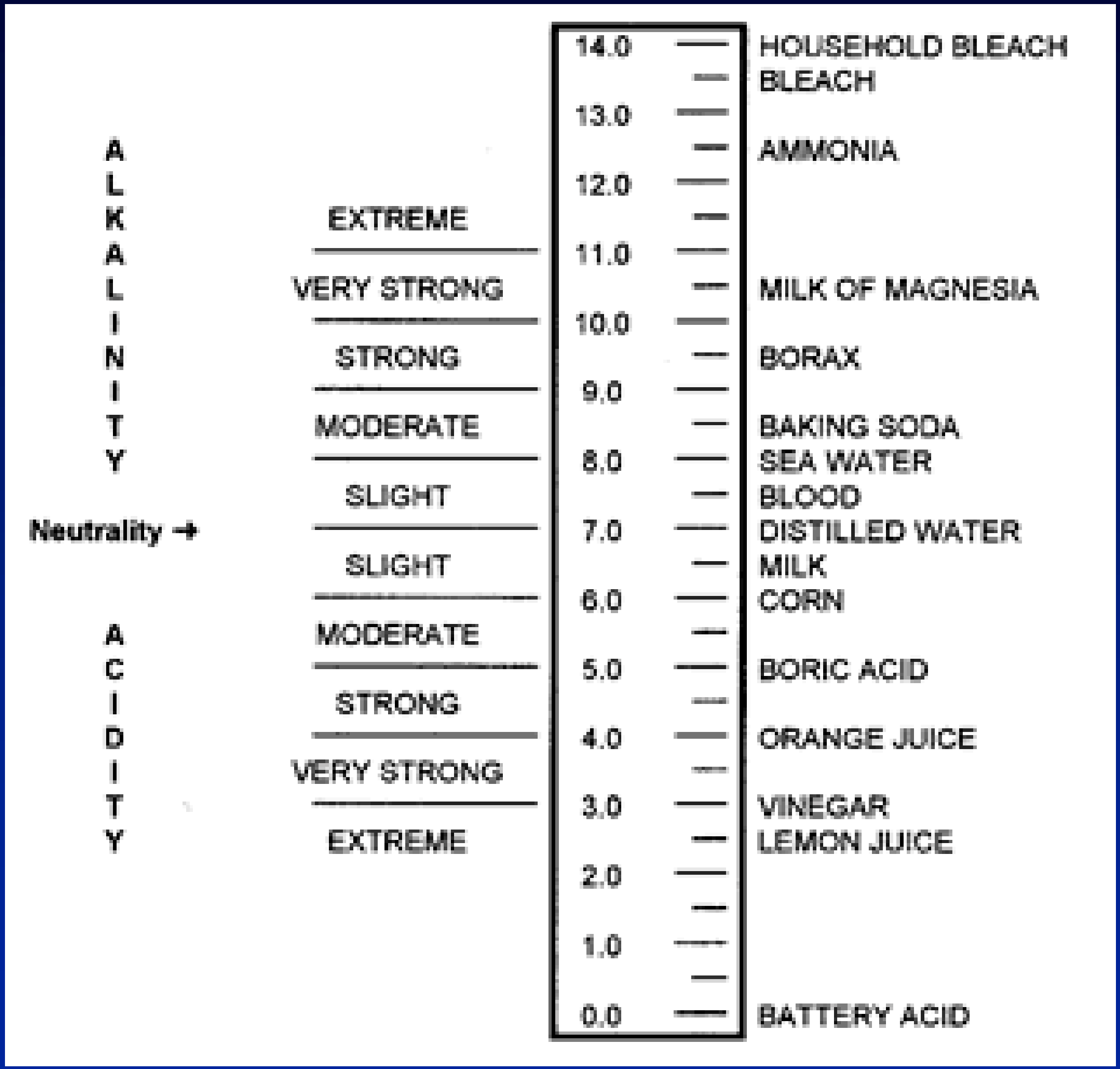
Inductive (non-contact, electrodeless, toroidal) Conductivity Sensor

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**

THORNTON / METTLER TOLEDO

pH Range


ALKALINITY
Neutrality
ACIDITY
EXTREME
VERY STRONG
STRONG
MODERATE
SLIGHT
SLIGHT
MODERATE
STRONG
VERY STRONG
EXTREME
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
HOUSEHOLD BLEACH
BLEACH
AMMONIA
MILK OF MAGNESIA
BORAX
BAKING SODA
SEA WATER
BLOOD
DISTILLED WATER
MILK
CORN
BORIC ACID
ORANGE JUICE
VINEGAR
LEMON JUICE
BATTERY ACID

pH Measurement

Dissociation of water

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

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

pH Scale

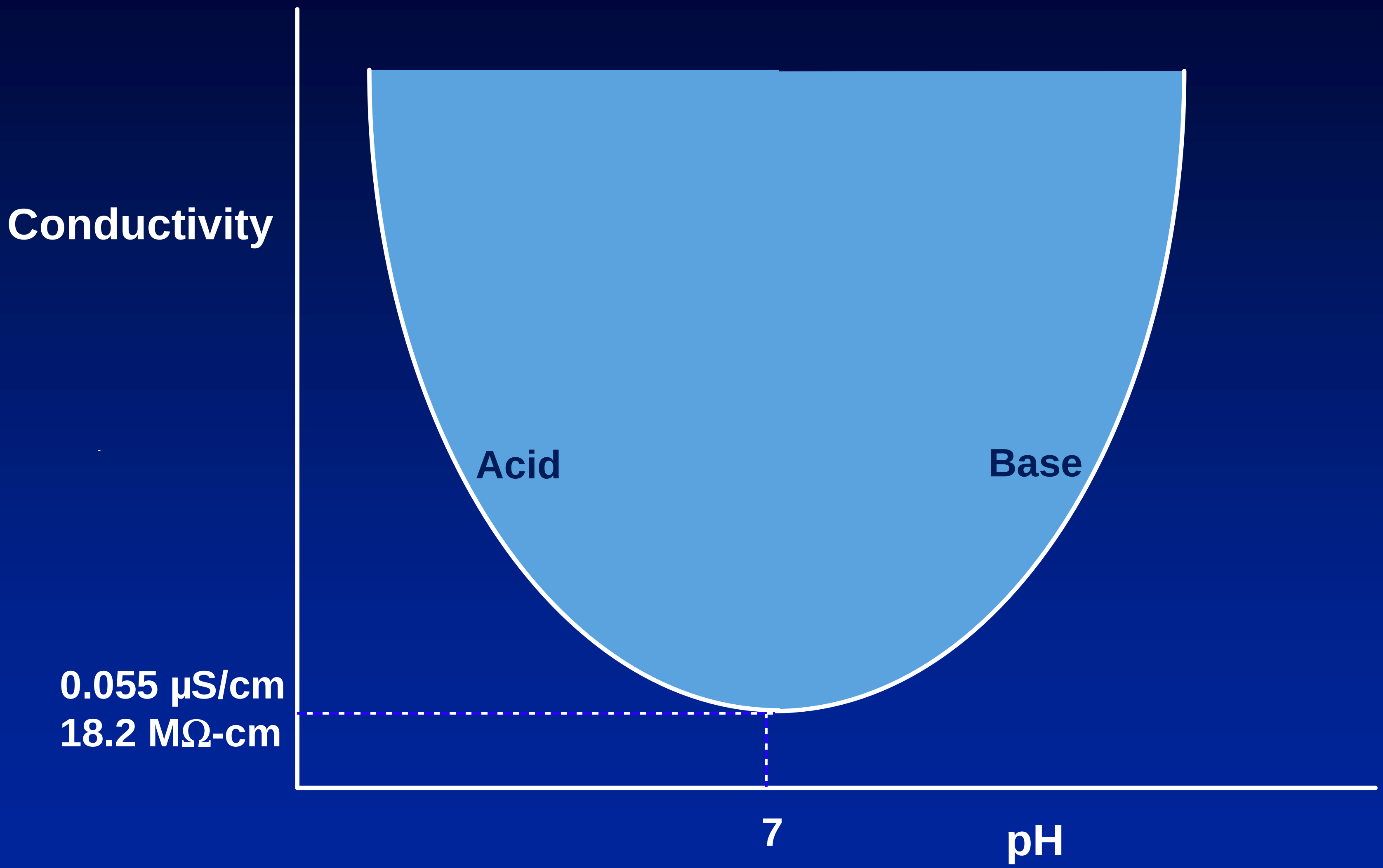
$$pH \sim -\log_{10} [H^+]$$

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

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}	$[OH^+]$

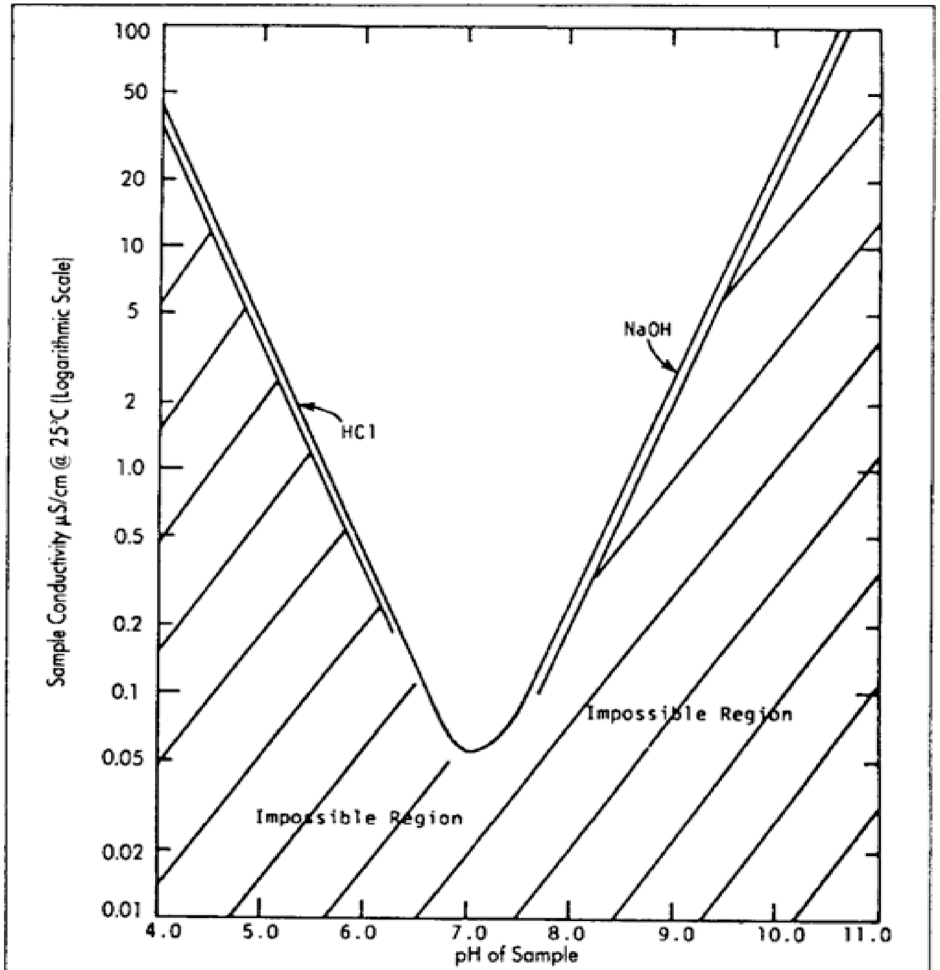
at 25°C

Conductivity vs pH



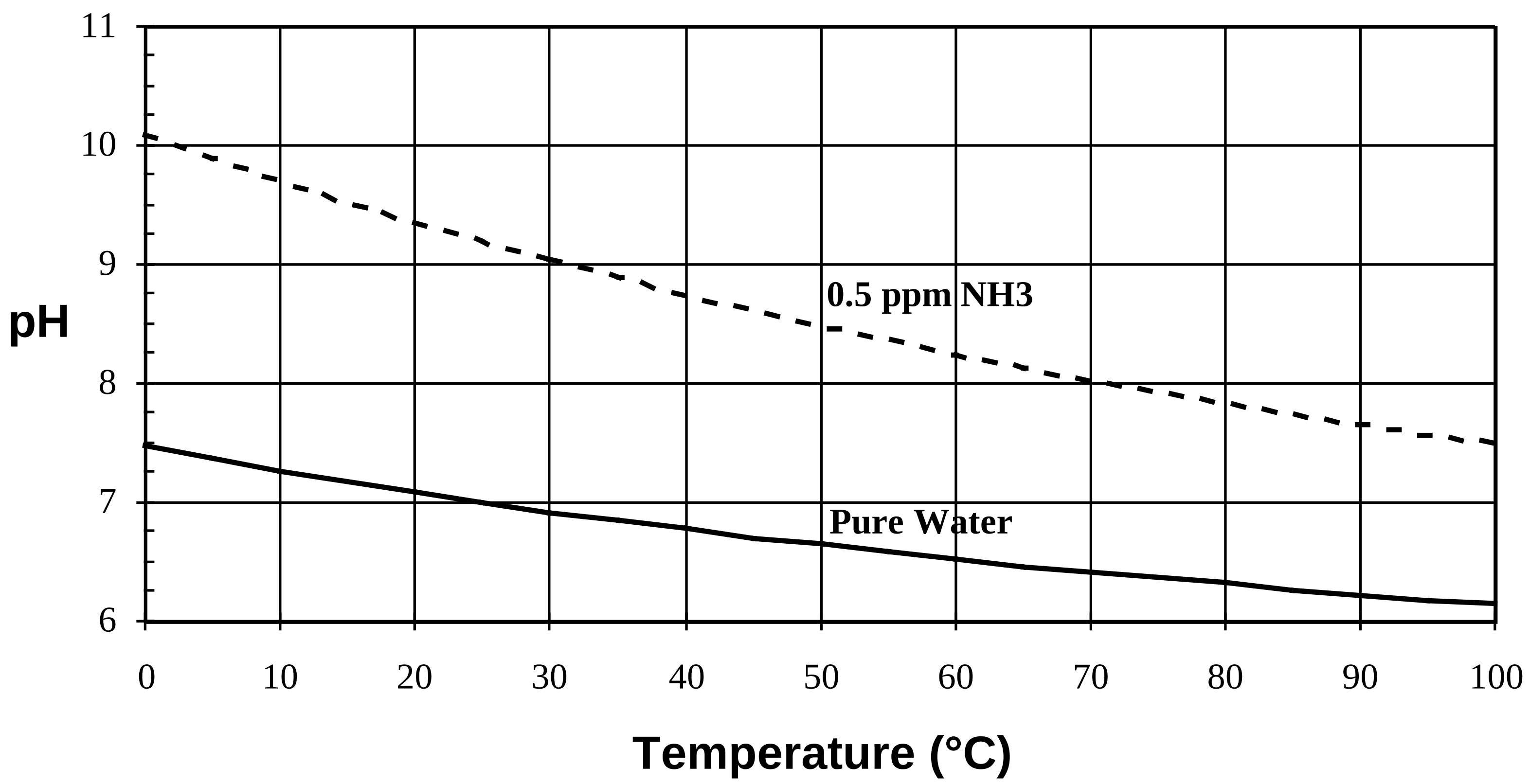
THORNTON / METTLER TOLEDO

Conductivity vs pH



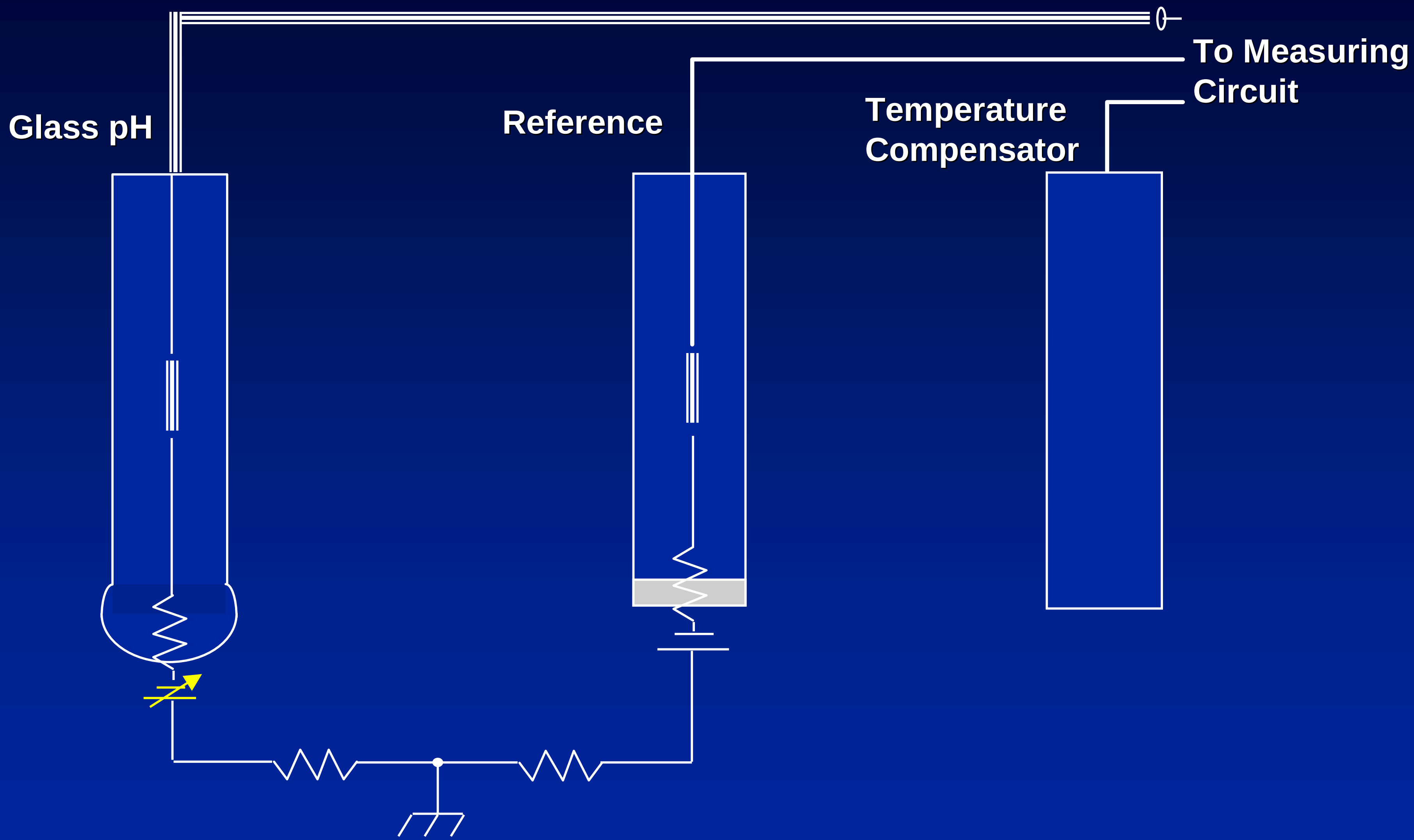
(Courtesy EPRI, NP-35891).

pH vs. Temperature for Pure Waters



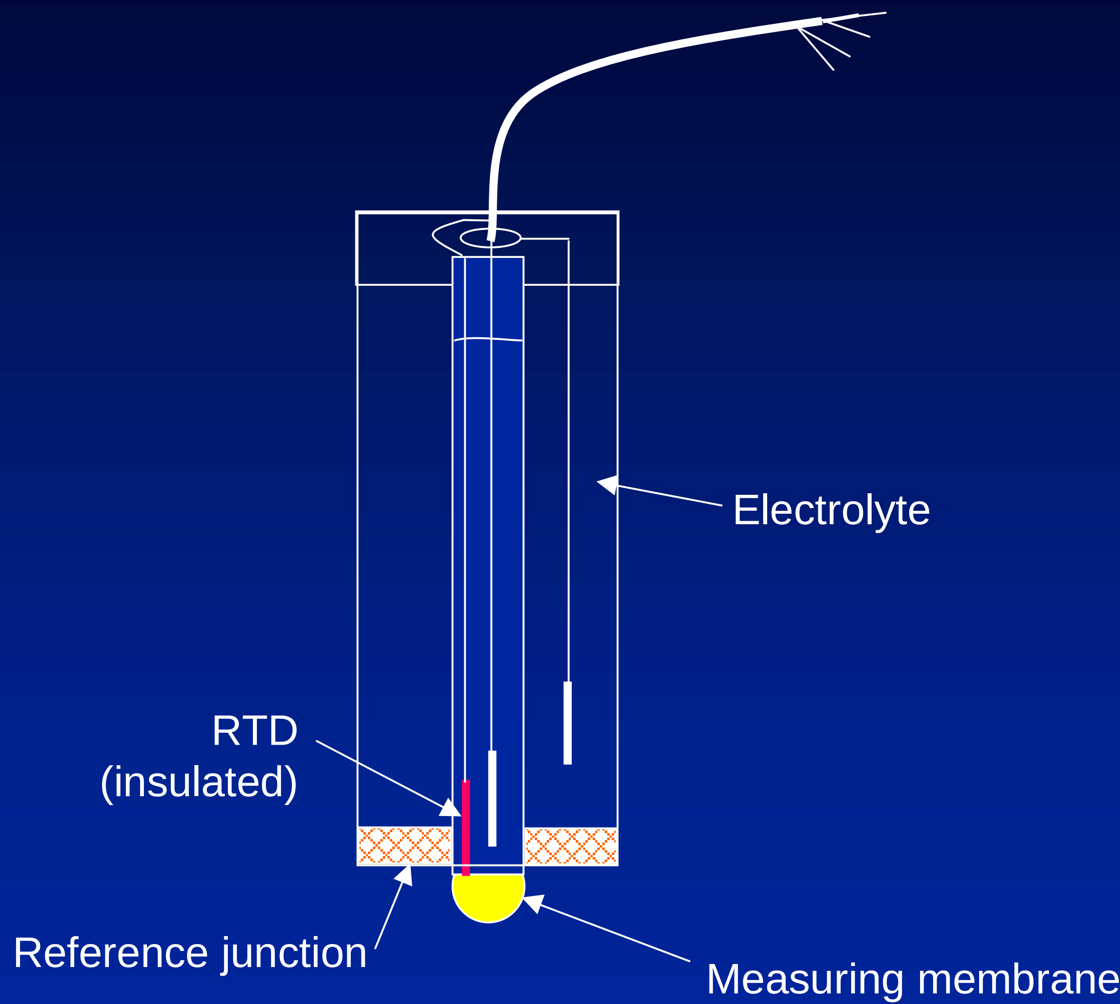
THORNTON / METTLER TOLEDO

pH Electrode System

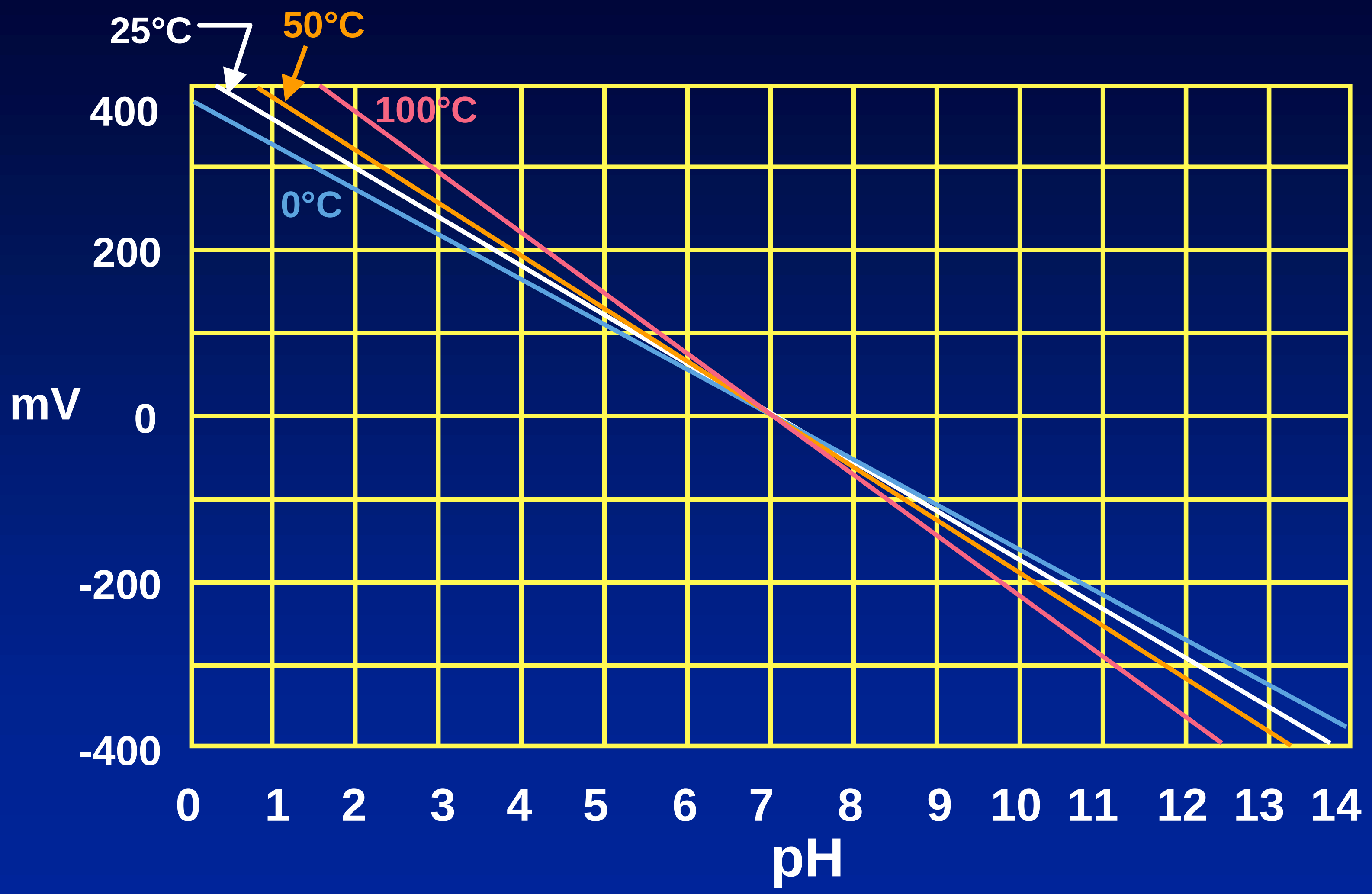


THORNTON / METTLER TOLEDO

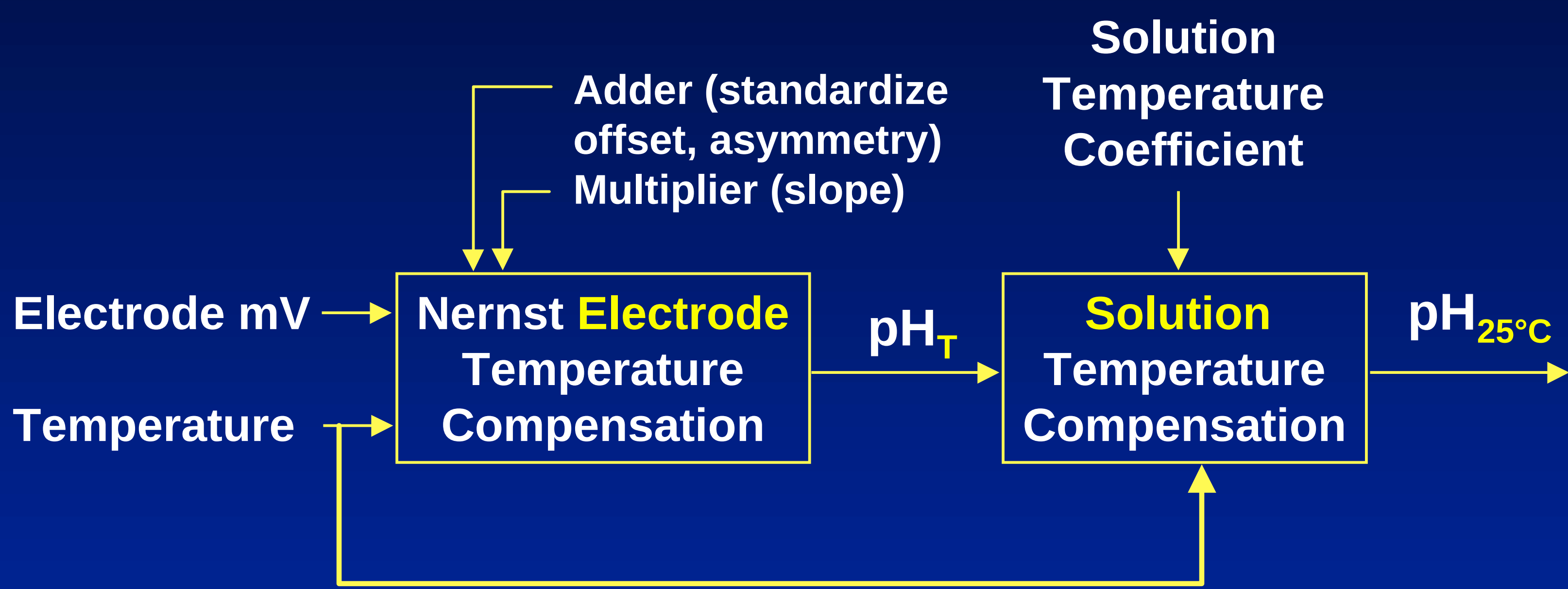
Combination pH Electrode



pH Electrode Output



pH Temperature Compensation



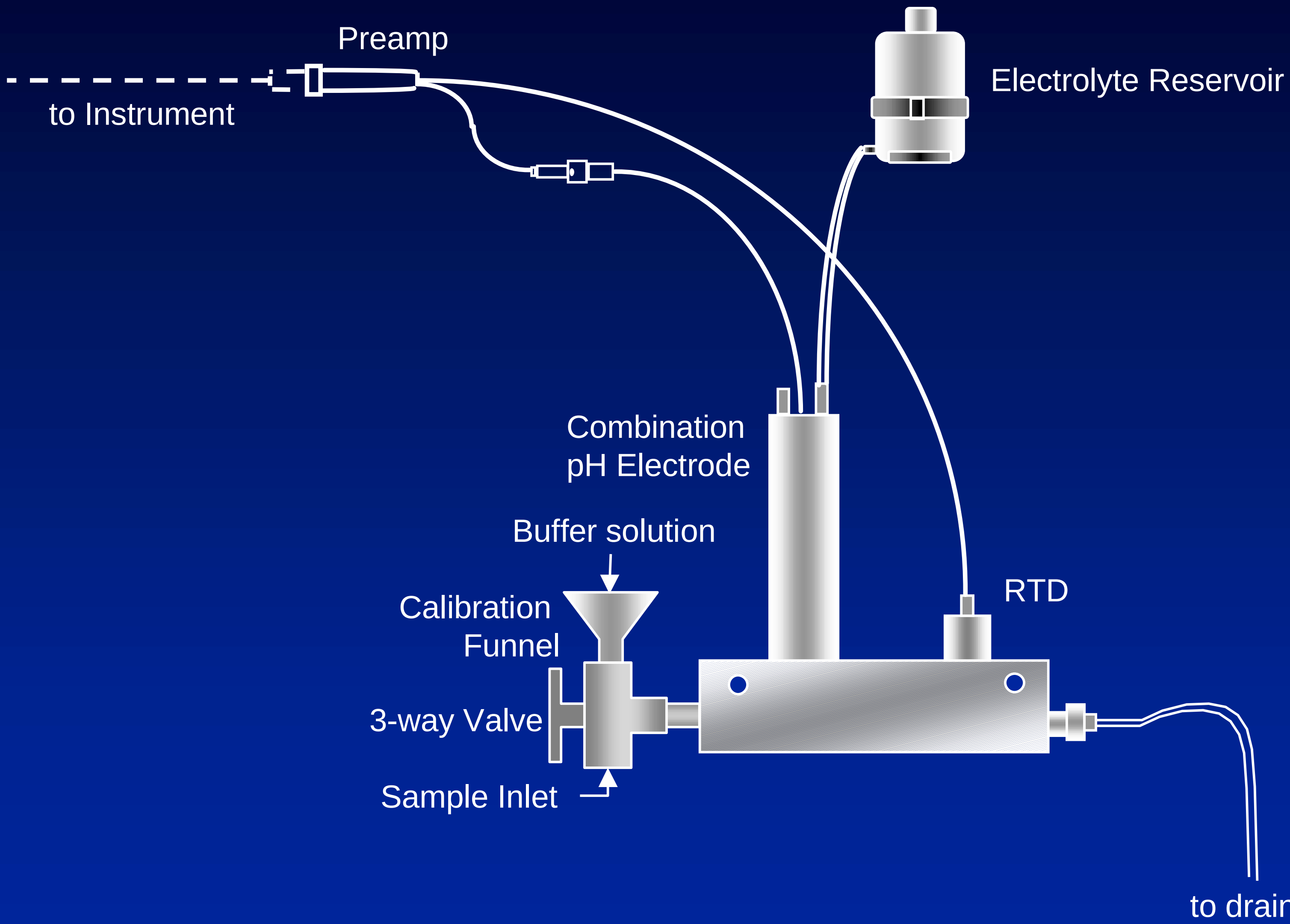
Detachable pH Electrode System

VP Preamplifier

VP pH Electrode

Housing

High Purity pH Sensor Assembly



THORNTON / METTLER TOLEDO

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

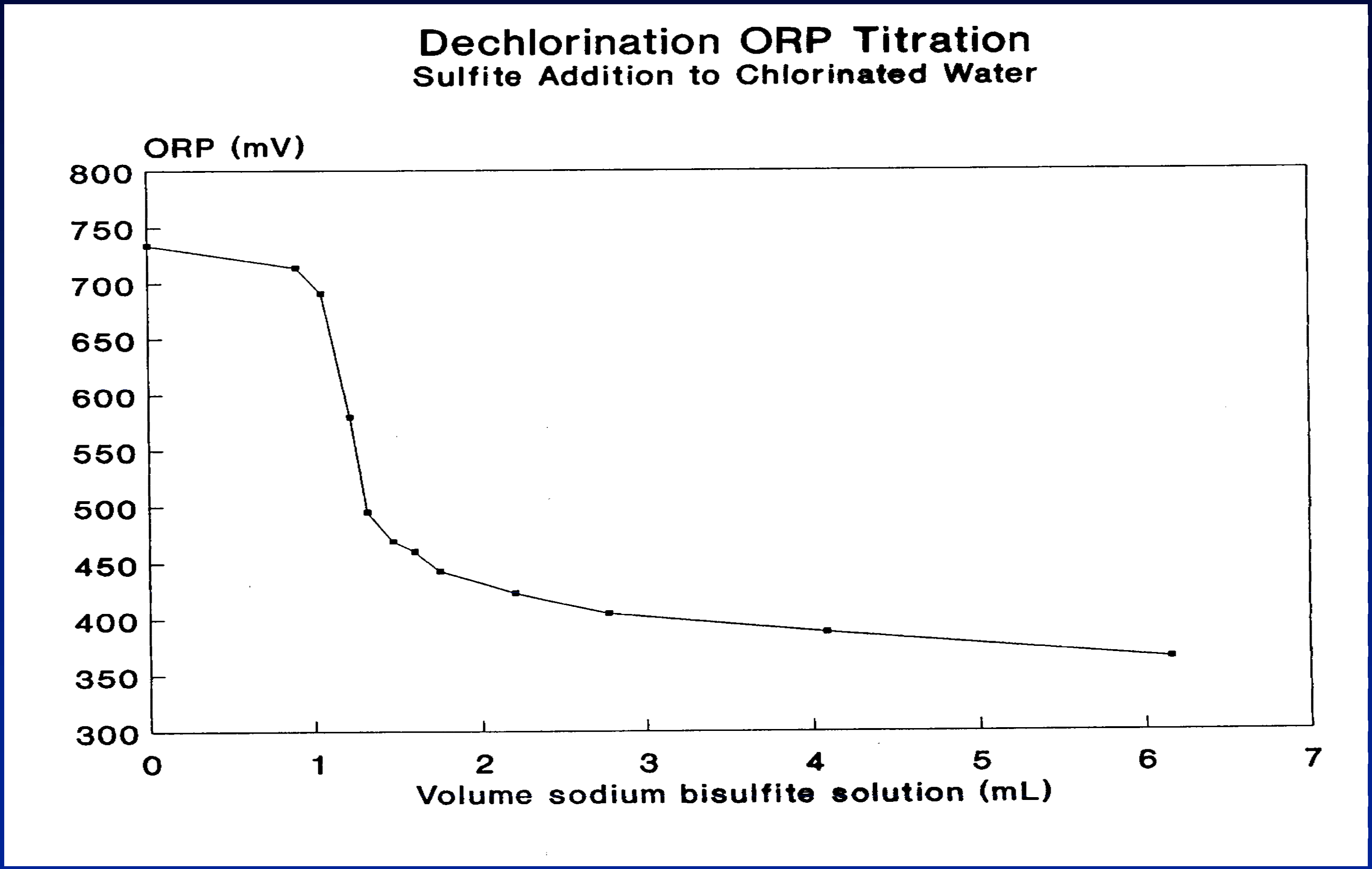
High Purity pH Measurement Equipment

- **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