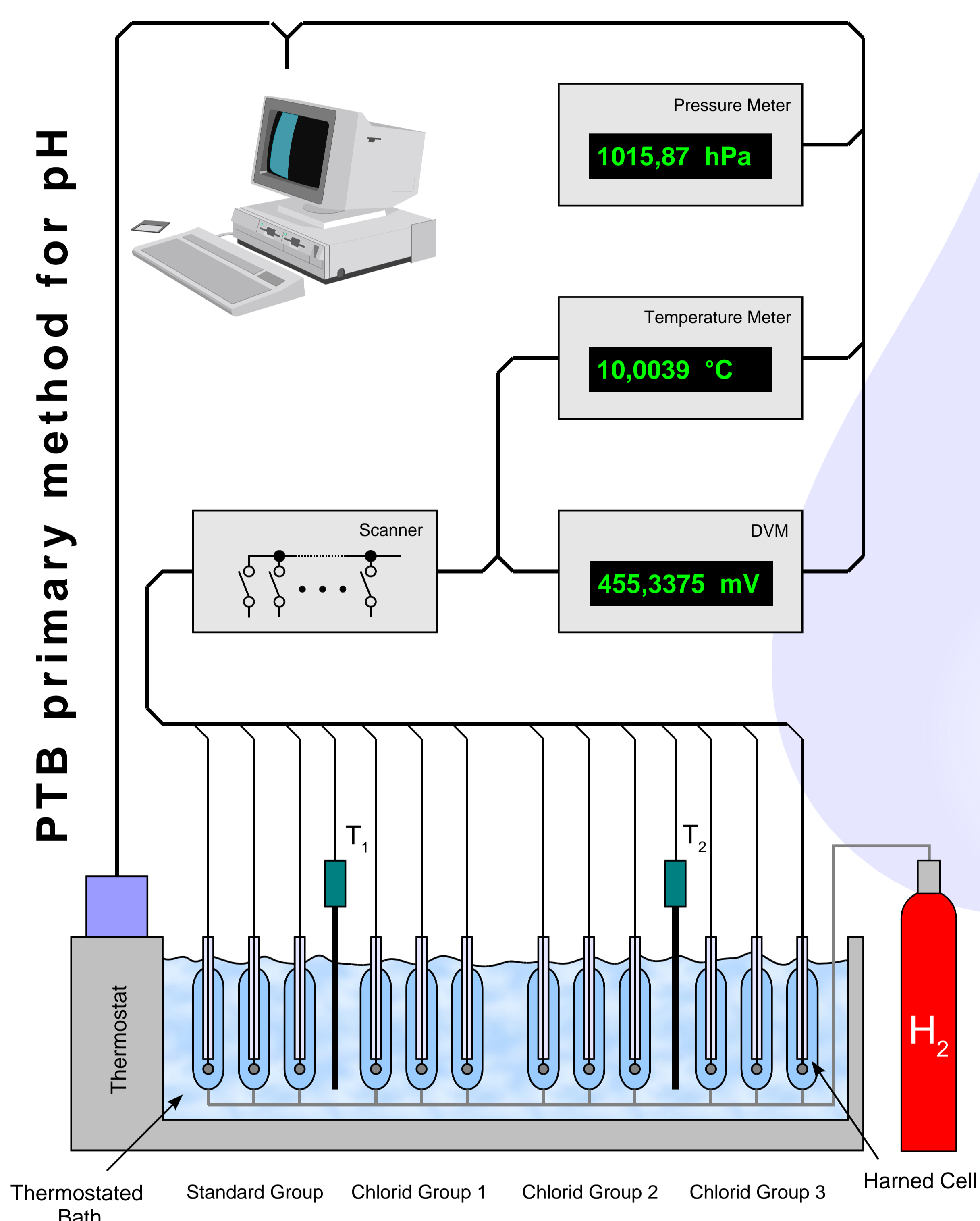


3.202 Metrology in Electrochemistry

Motivation

- pH is a measure of the acidity of solutions
- For pH traceability does not extend to the SI **Single ion activity coefficient!**
- Primary pH standards related as closely as possible to the definition of pH and provisions for their dissemination to the field level are the prerequisite for the comparability of sample pH values

How to realize?



The primary method for pH:

Harned cell: $\text{Pt} | \text{H}_2 | \text{buffer}, \text{Cl}^- | \text{AgCl} | \text{Ag}$

- Cl^- are added to stabilize the potential of the Ag/AgCl electrode
- The potential difference E :

$$E = E_0 - k \lg(a_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\text{Cl}^-}) \quad k = R T \ln 10 / F$$

- a activity
- m molality
- γ activity coefficient
- E_0 standard potential of the Ag/AgCl electrode.

- Rearranged to give the acidity function p_a :
 p_a is measured as a function of m_{Cl^-}
 $p_a = -\lg(a_{\text{H}^+} \gamma_{\text{Cl}^-}) = E - E^0 / k + \lg(m_{\text{Cl}^-})$,
- p_a is extrapolated to zero chloride molality.
 $p_{a_0} = -\lg(a_{\text{H}^+} \gamma_{\text{Cl}^-})_{m_{\text{Cl}^-} \rightarrow 0}$
- γ_{Cl^-} is obtained by the Bates-Guggenheim convention:
The ion size parameter of the Debye-Hückel theory at low ionic strength ($I < 0.1 \text{ mol kg}^{-1}$) is set equal to 1.5
- $\text{pH} = p_{a_0} + \gamma_{\text{Cl}^-}$

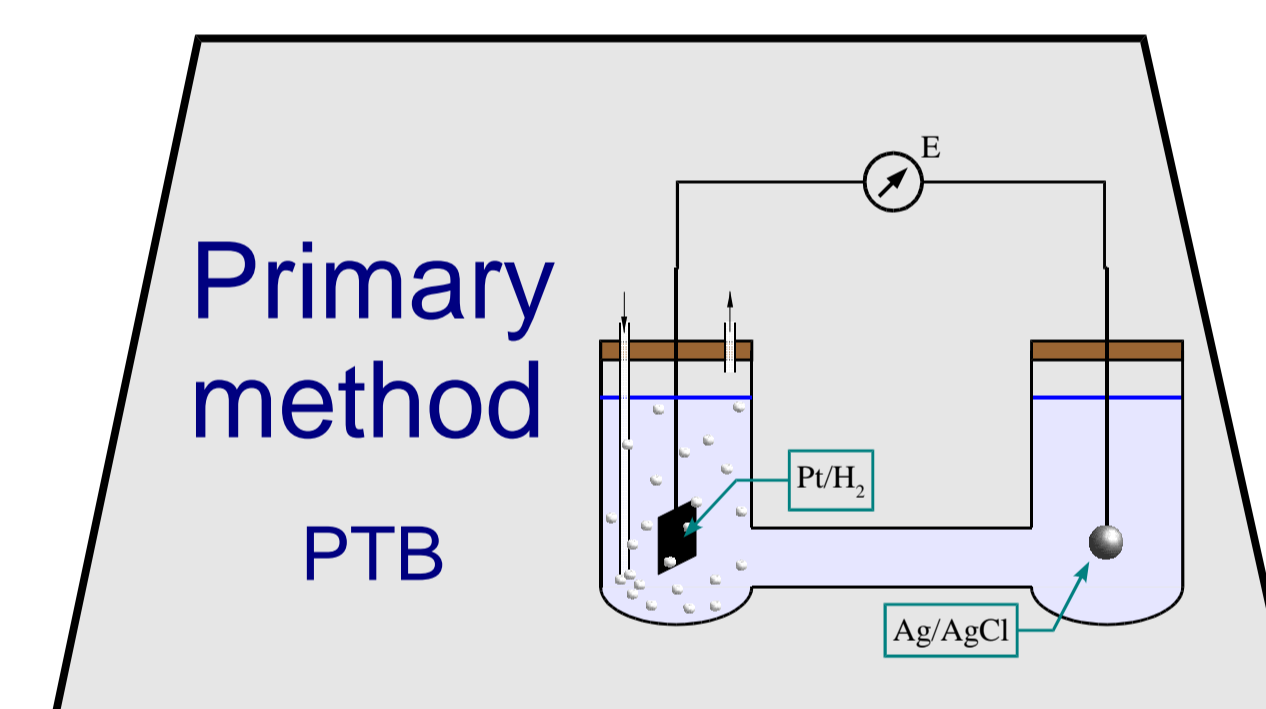
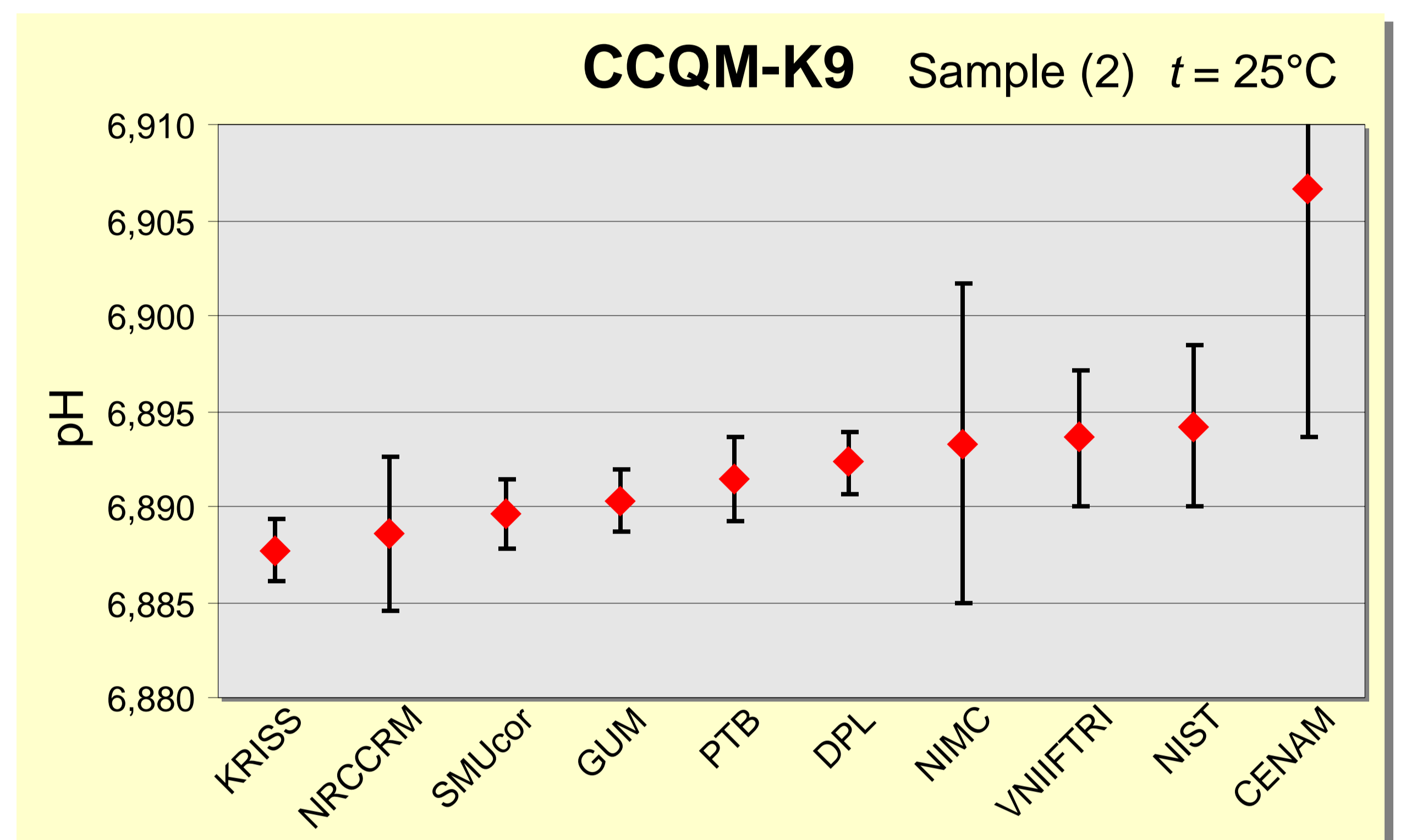
Aim

To establish a traceability chain in Germany based on a primary method for pH

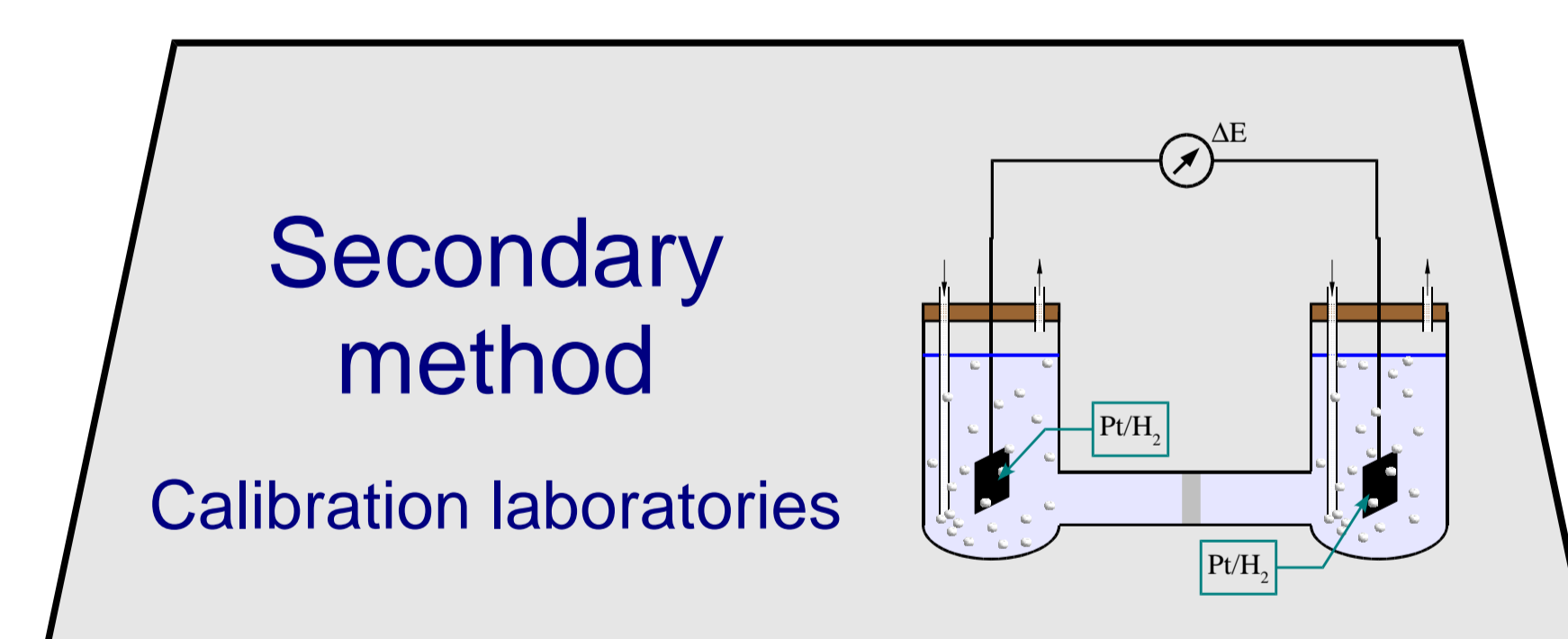
International comparisons:

pH determination by Harned cell measurements

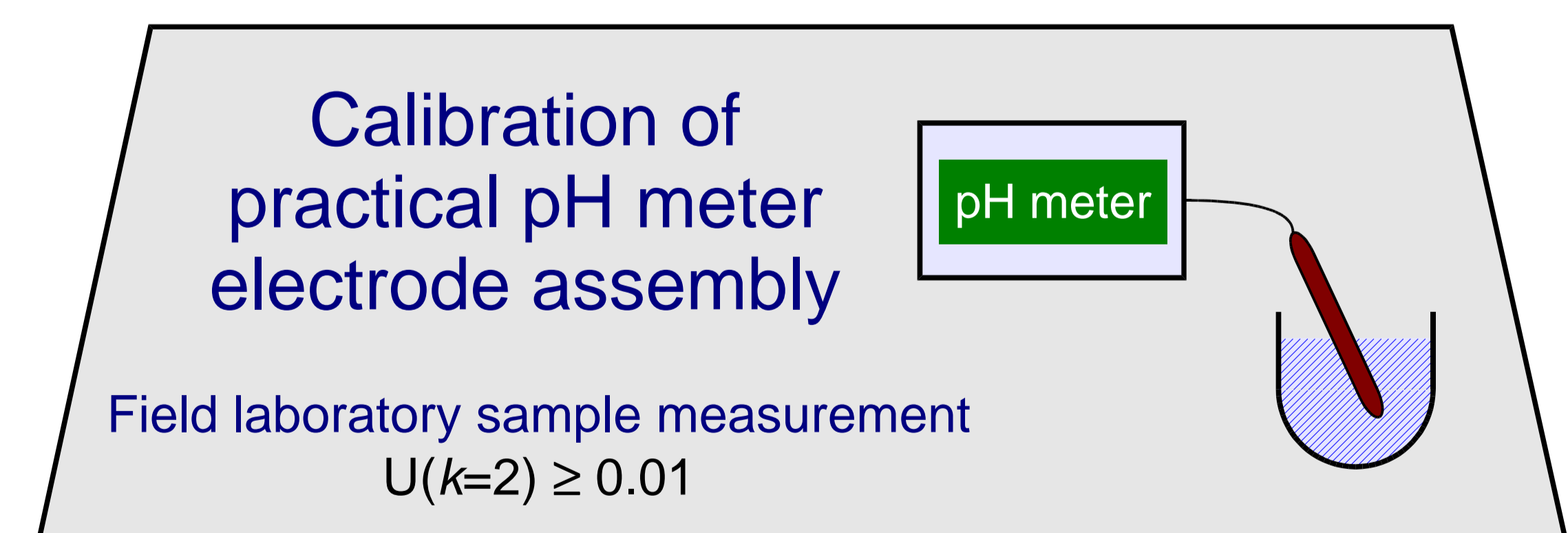
- CCQM-K9 in 2000 <http://www.bipm.fr>
- CCQM-K17 started in 2001
- EUROMET 300, 370, 424 <http://www.euromet.ch>
- PTB has been the pilot lab for all comparisons



Primary buffer solution
 $U(k=2) = 0.002$



Secondary buffer solution
 $U(k=2) = 0.003$



Field laboratory sample measurement
 $U(k=2) \geq 0.01$

Future work

Extension into media of ionic strength $I > 0.1 \text{ mol kg}^{-1}$ and to complex matrices