TECHNICAL NOTE

Electrochemistry July 2014

pH probes with Red Rod technology

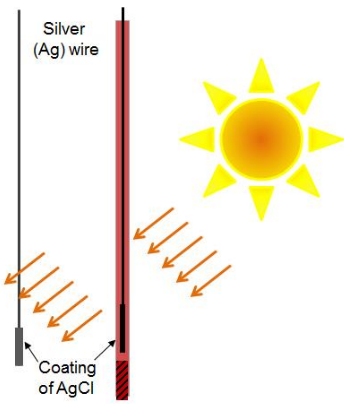
Red tubes inside the probe

Looking at a Red Rod pH probe, the first visible difference from “standard” pH probes is the two inner red glass tubes.

What is their purpose?

The standard reference system comprises a combination of silver wire (Ag) and silver chloride (AgCl) in equilibrium:

$AgCl \leftrightarrow Ag^+ + Cl^-$,



The status of the equilibrium depends on AgCl, Silver and Chloride ions. If one side of the reaction changes, the equilibrium changes as well. Therefore the reference element is no longer stable, identified by a changing reference potential and a shorter lifetime.

Ambient light, especially the daylight, reacts continuously with AgCl and reduces traces of silver ion to silver metal. This reduces the lifetime of the probe.

$$AgCl \leftrightarrow Ag^+ + Cl^-$$

$$AgCl + [\textit{UV light}] \leftrightarrow 2\ Ag\downarrow + Cl_2 \uparrow$$

With red colored glass tubes protecting the reference system, the effect of UV light is almost zero and the reference systems remains stable over a long period of time.

Saturated KCl filling

The standard filling solution for pH probes is 3 molar KCl. Inspection of the internal filling solution, does not provide any indication for the user if the 3 molar solution becomes diluted by sample down to 2.8 molar or 2.5 molar. The clean liquid inside the probe gives no hint of changes in the electrolyte solution, except if the fill level is low.

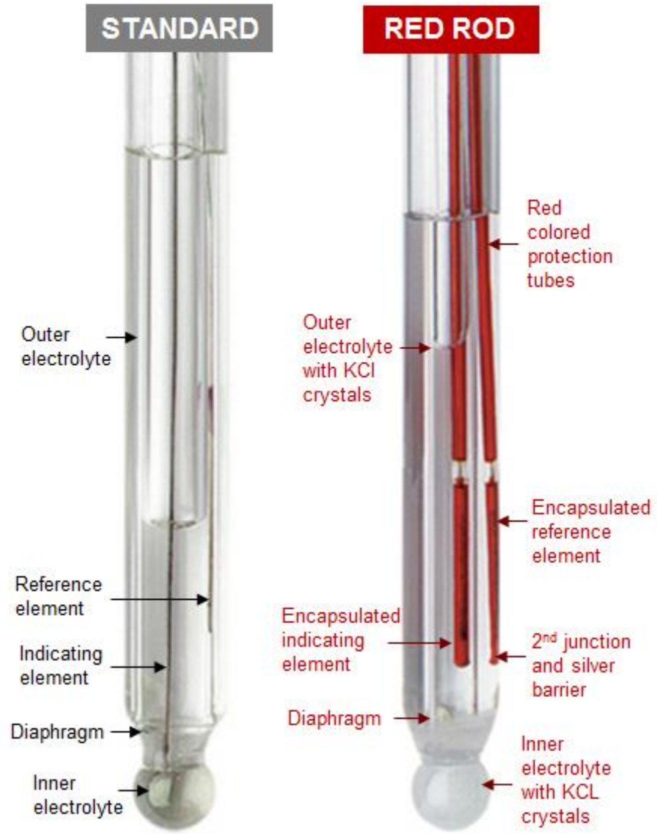
Saturated KCl has a visual indicator that it is saturated: the KCl crystals. As long as KCl crystals can be seen inside the pH probe, the solution is saturated.

Additional KCl crystals

Red Rod pH probes have a higher temperature limit (100 / 110°C) because of the glass housing and especially because of the saturated KCl electrolyte.

With increasing temperature the solubility of KCl changes and KCl crystals can dissolve, still maintaining a saturated solution. When cooling down, crystals can grow again and re-built the visual indicator for saturated KCl electrolyte solutions.

Red Rod pH probes are filled with saturated KCl solution and have additional KCl crystals inside the reference area and inside the pH glass bulb.



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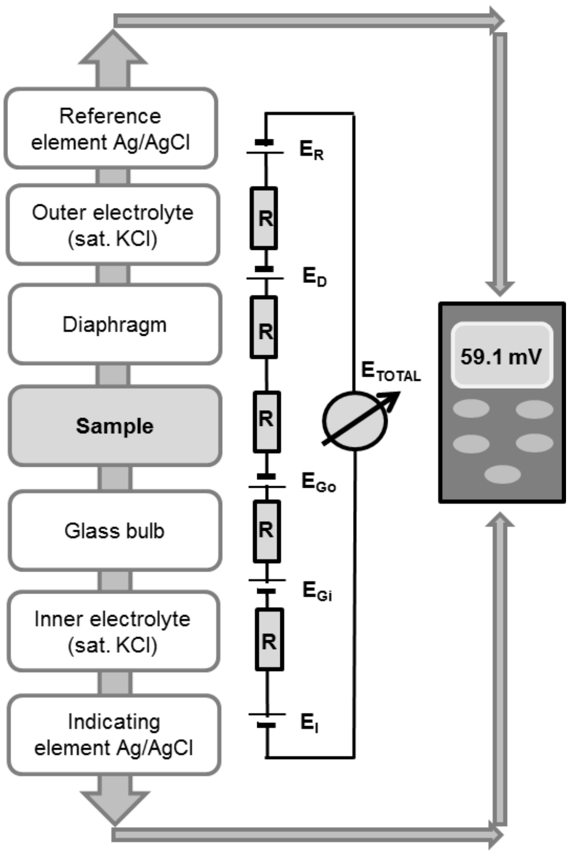
Symmetrical Reference System

Usually a combined pH probe has a pair of Ag/AgCl electrodes inside (reference system and indicating element). Standard pH probes have just "simple" Ag wire coated with AgCl, which is in direct contact with the electrolyte solution. Due to variations in manufacturing of these Ag/AgCl electrodes, most of the Ag/AgCl pairs are not really equal and they tend to be "not symmetric". This causes an **Asymmetry Potential ≠ zero mV**.

Ideally both are made equally (see graphic with Red Rod Technology) and the **Asymmetry Potential = zero mV.** Symmetric pairs of reference and indicating elements as provided by Red Rod probes show similar aging effects and do not add varying potentials to the system.

pH measurement as electrical circuit

If we consider all elements of a pH measuring system in contact with sample we can replace each one with electrical components such as resistors. At each resistor point a certain potential can be measured. The combined potential gives the measurement potential displayed on the pH meter, which is converted into a pH values, using the calibration data.



E_R : reference potential in contact with inner electrolyte
E_D: potential formed at the diaphragm
E_{Go}: potential at the outer glass bulb with sample
E_{Gi}: potential at the inner glass bulb with electrolyte
E_i : potential of the indicating element with electrolyte
R: sum of resistors and capacitors for this part

All potentials add to the E_{TOTAL} potential, displayed on the pH meter.
With standard reference & indicating elements their potentials may vary over time and at different rates. E.g. the reference element potential may change more quickly than the inner indicating element resulting in a significant increase of the asymmetry potential over time.

With Red Rod pH probes all potentials are stable and accurate and reproducible pH measurement can be performed.

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