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TECHNICAL NOTE

Electrochemistry

November 2013



What are the individual parts of a pH electrode?

Glass bulb / indicator element

The glass electrode consists of a bulb of pH sensitive glass, filled with potassium chloride (3 molar or saturated) pH=7. Within the glass bulb a silver wire coated with silver chloride (AgCl) is placed in KCl solution. Between the inner (pH neutral) glass layer and the outer, which is in contact with the sample, a mV potential develops, which depends on the H⁺ concentration in the sample. With variation of the outer H⁺ concentration the potential adjusts reproducible between reference and glass (indicator) electrode. Therefore this electrode combination allows measuring the H⁺ concentration, what is equal the pH value.

The pH independent reference element

The reference element (Ag/AgCl) is in an electrolyte solution (KCl 3 molar or saturated). As long as this situation of reference element / electrolyte solution is kept optimal, a stable reference potential forms, which depends on temperature (and Cl concentration) only. Against this reference potential the potential of the glass electrode is measured.

The electrolyte solution

To maintain a constant potential of the Ag/AgCl electrode an electrolyte solution is needed, which has sufficient chloride ions (Cl⁻) and which is pH-neutral. Commonly used are KCl solutions, which are 3 molar or saturated. With gel filled electrodes there is sufficient potassium chloride in the gel. Refillable electrodes must be regularly controlled and refilled, because the fill level is important for the electrolyte outflow through the diaphragm.

The diaphragm

The connection between reference electrode and the sample solution goes through the diaphragm. Normally it lets electrolyte solution flow out, but hinders samples to get inside. Therefore the reference electrode maintains a constant environment (ion concentration, potential).

If sample comes into the inner electrode, the chloride concentration changes and therefore the equilibrium

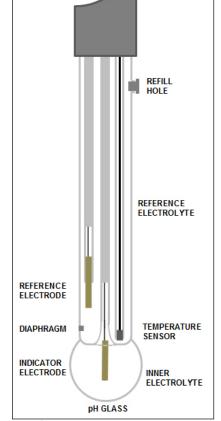
between Ag and AgCI. A shift of the reference potential or even a damage of the electrode can be the result.

Types of diaphragms:

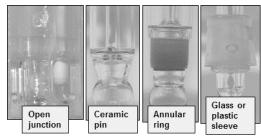
- ⊕ open hole
- ⊕ ring opening
- ⊕ ceramic pin(s)
- ⊕ ceramic disk
- Plastic fiber bundle
- Platinum bundle
- ⊕ PTFE ring
- Glass fritte ring
- Sleeve (glass / PTFE) and core (glass)

The temperature sensor

Most pH electrodes have an integrated temperature sensor, which measures in parallel to the mV signal.



the temperature of the electrode / sample solution. This is needed during calibration (temperature dependence of pH buffer solutions) and during sample measurement. Modern pH meters do this automatically. Is no temperature sensor integrated, a separate sensor must be used and connected to the pH-Meter.



Examples of diaphragms

HACH-LANGE GMBH

Willstätterstr. 11 40549 Düsseldorf Tel.:+49 211 52880 Email: info@hach-lange.de