Well advised with Roth.

pH measurement – Information and interesting facts

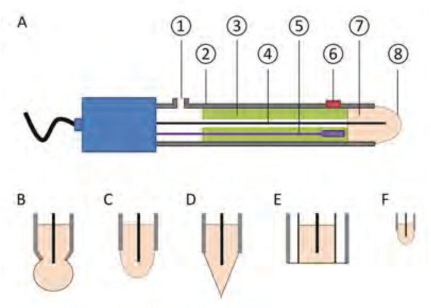

Fig.:
A: Longitudinal section through a pH single-rod measuring cell:
① Filler neck, ② Electrode,③ Reference electrolyte, ④ Outlet, ⑤ Reference outlet, ⑥ Diaphragm,
⑦ Internal buffer, ⑧ pH-sensitive glass membrane
B-F: Application-specific types of pH-sensitive glass membrane

Choosing the right pH single-rod measuring cell

During the pH measurement a pH single-rod measuring cell (see Fig. A) is inserted into the sample solution in such a way that the pH-sensitive glass membrane interacts with the hydrogen ions ("protons") in the sample solution. The resultant voltage potential is dependent on the concentration and is measured by the measuring instrument and converted to a pH value.

pH single-rod measuring cells are distinguished, among other things, by the reference electrolyte, the diaphragms, the shape of the glass membrane and the electrode material (glass or plastic). The sample solution dictates which electrode is most suitable for the pH measurement.

The **reference electrolyte** is stored inside the pH single-rod measuring cell. It is in contact with the sample solution via a special connection, the so-called diaphragm, and can flow into the sample solution in a controlled manner. Reference electrolytes are roughly subdivided into two categories - liquid electrolytes and gel electrolytes.

- pH single-rod measuring cells containing **liquid electrolyte** have a faster response time, greater measurement certainty and longer life. The electrolyte is refillable, but is also completely exchangeable and more heat resistant.
- pH single-rod measuring cells containing **gel electrolyte** incur virtually no loss of electrolyte during the measurement and do not need to be refilled. They are rugged, require little maintenance and affordable, but they are unsuitable for highly acidic/basic solutions with a low ion content.

The connection between the electrolyte and the sample solution is made in a different way. It is important that the diaphragm doesn't become clogged by the sample solution (e.g. by viscous solutions, suspensions, aqueous samples with a high protein content), as otherwise it will not be possible to obtain a correct pH measurement.

- The **ceramic diaphragm** has a porous structure which has a high chemical resistance, but is highly sensitive to contamination. This diaphragm is suitable for standard measurements in aqueous solutions which are free of suspended matter.
- The **platinum diaphragm** consists of fine, smooth platinum wires which are twisted together and fused into the glass shaft of the pH single-rod measuring cell. The electrolyte flows out through cavities between the platinum wires. The platinum diaphragm does not clog up as quickly as the ceramic diaphragm, but it is unsuitable for sample solutions with a strong oxidising or reducing effect.
- The **fibre diaphragm** is similar to the platinum diaphragm, but is less chemically stable. It comprises a non-metallic fibre bundle (e.g. made of nylon) and often contains a gel electrolyte.
- The **ground joint diaphragm** is suitable for measuring pH in contaminated solutions, sludge, suspensions, emulsions and viscous media. The bottom section of the electrode is ground and covered by a sleeve. The electrolyte flows out from the fine gap between the shaft and sleeve at a high velocity. This also allows the pH of sample solutions with a low ion content to be measured. The diaphragm can be cleaned very easily by pushing up the sleeve.
- The **hole diaphragm** is a small connecting hole between the gel electrolytes and the sample medium. This diaphragm is highly resistant to clogging because it does not have a reticular structure.

Depending on application, the pH-sensitive glass membrane is shaped in a specific way (see Fig. B-F).

- For standard applications, the glass membrane has either a **spherical** structure (B) or a **hemispherical** structure (C).
- For insertion measurements in semi-solid, pasty and solid samples, the glass membrane is **tapered** (D).
- For surface measurements and droplet-sized samples, the glass membrane is **flat** (E).
- For small quantities of fluid and sample solutions in narrow vessels, there is a micro version in which the glass membrane is **narrow** and **hemispherical** (F).

Temperature compensation

One of the key factors influencing pH measurements is the temperature. For this reason, only pH values which have been measured at the same temperature should be compared with one another. In order to correlate the pH value with the actual temperature of the sample solution, temperature compensation should be carried out. The temperature can either be entered manually into the pH meter or measured automatically by an additional temperature sensor.

Calibration

A pH single-rod measuring cell is characterised by its zero point and its slope. At a pH of 7 the electrical voltage at the zero point is approx. 0 mV. The slope describes the change of voltage between two pH units. Since these characteristics change as a function of time, the sensor should be calibrated regularly using a calibration solution with a known pH. This is particularly important **after cleaning, maintenance or long periods of storage** of the pH electrode. To obtain more exact test results, **2-point calibration** should be carried out at least once and the **pH buffer solutions is use should have a pH nearest to the expected pH values**.

Storage

pH single-rod measuring cells are stored in an **aqueous, solution with a high ion content**. A solution which matches the inner electrolyte is recommended. The pH 4 buffer solution can be used as an alternative. However, pH single-rod measuring cells should never be stored in distilled water.

For longer periods of storage (several weeks to months), pH single-rod measuring cells can also be stored in a dry state. The electrodes will age more slowly as a result, but the outer hydrated layer on the pH-sensitive glass membrane which forms through contact with aqueous solutions will be irreparably damaged. Therefore, pH single-rod measuring cells which have been stored in a dry state have to be wetted again prior to initial use. For this purpose, the pH single-rod measuring cell is regenerated overnight in the storage solution.

Care and maintenance

With proper care and maintenance, pH single-rod measuring cells will deliver more exact measurement results, shorter response times and last longer.

- After each measurement the electrode must be flushed with deionised water and stored in the storage solution. If the electrode is dabbed with a paper towel, its rough surface should not come into contact with the pH-sensitive glass membrane.
- pH single-rod measuring cells containing liquid electrolyte have to be refilled. It is important that the electrolyte level does not drop below that of the sample solution because it will otherwise flow into the electrode.
- To prevent crystallisation of the electrolyte, the electrolyte should be completely exchanged on a regular basis.
- If air bubbles form inside the measuring cell, they can be removed by carefully shaking the electrode. Air trapped in the vicinity of the glass membrane leads to unstable measurement values.
- If the electrodes or the diaphragm are contaminated, various cleaning solutions can be used.

Useful life

The pH single-rod measuring cell is a **consumable subject** to diminishing performance over time. Its useful life is considerably reduced by high temperatures (>50 °C) and measurements at extreme pH values in particular. However, the type of sample solution, duration and frequency of measurement and, not least, electrode maintenance are also factors which influence the useful life of the measuring cell. Ageing symptoms include longer response time, decreasing slope and zero shift.

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