Quick guide to pH measurement problems

Measuring pH correctly hides many pitfalls.
In those few pages we will have a look on which are control procedures to define the reasons for possible malfunctions in the pH chain.

pH measurement chain

pH-meter

Cable

pH electrode

Temperature probe

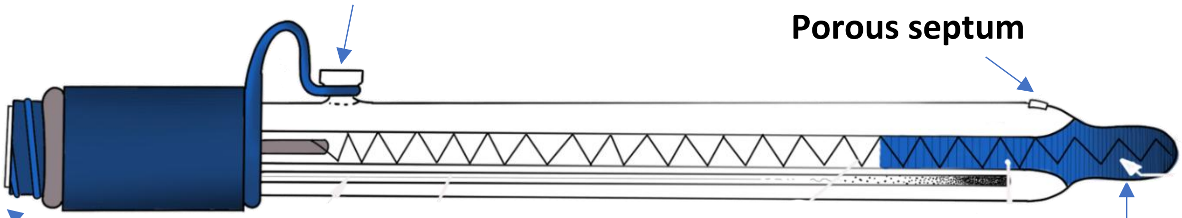
Buffer solutions

Critical points

Buffer solutions: if expired or polluted, they can prejudice the whole chain.
Connectors: in a moist environment they can oxidize.
Cable: assimilate moisture - subject to strong stress from use.
pH electrode: explained in detail below.

Life of an electrode

Even if unused, pH electrode loses its potential progressively over time.
Average life of a properly used electrode is 18 months.
High temperatures, samples with a pH lower than 2 or greater than 10 can shorten life of an electrode even for many months.
Cable and buffer solutions also incline to deteriorate.



Operation

pH electrode detects an electrical intensity (mV), the pH-meter converts it to a pH measurement.
Soak the electrode in pH 7.00 and in pH 4.01 solutions, washing electrode in water and drying it carefully between the two solutions. Switch to mV mode on the pH-meter.
If everything works correctly, values to read are:

pH 7.00 = 0 mV (± 30 mV)

pH 4.01 = 177 mV (± 30 mV)

Indicator parameters are slope (%) e offset (mV).
The slope is given by the difference in mV measured between the two solutions with a known value: 177 mV of difference amount to 100% of slope (optimal value).
The offset indicates how much the measured mV values deviate from the optimal values in pH 7.00 (keeping the slope).

Electrode malfunction

Measure the mV in buffer solution pH 7.00 and pH 4.01.
If the electrode has a problem, we will find one or more of the following cases:

- **Low Slope** (< 130 mV difference).
- **Slope 0%** (< 10 mV difference).
- **Shift Offset**: the slope is good, but the mV scale is shifted (pH 7.00 = 40 mV – pH 4.01 = 217 mV).

Low Slope

Low slope problems normally affect the membrane. Occurs when:

- **Dirty membrane**: oily or oily residues can patinate the membrane, blinding it. Clean with HF **(maximum 30 seconds)**.
- **Storage** of the electrode in water: NEVER store the electrode in water, even a few hours may affect his membrane.
- **Air bubbles** in the membrane. Shake the electrode vigorously to remove them.
- **Electrode exhausted** due to normal life cycle.

Slope 0%

It occurs when in pH buffer solution pH 7.00 and pH 4.01 measure the same mV value (or two very close values).
Membrane Glass crack: Glass breaking near membrane welding. Normally visible only under a microscope (picture 3).
No communication between electrode and tool:

- Interruption of an electrical connection on the top S7 connector.
- Faulty connection cable.
- Faulty tool.

Offset

Correct slope (177 mv of difference between two buffers) but values other than 0 and 177.

Electrodes with liquid electrolyte:

- **Check that there is electrolyte inside the electrode.**
- **Check the porous septum**. Usually, it is white milk colour.

If clogged with proteins it will appear **yellow colour**.

Perform a cleaning with Protein cleaning solution (cod.32208093)

If clogged with metals, it will appear **black colour**.

Perform a cleaning with Diaphragm cleaning solution (cod.32208103)

Cleaning procedure:

leave the electrode immersed in the cleaning solution for one-night, next morning replace electrolyte inside electrode and store electrode in storage solution for 2 hours. After this time, the electrode will be ready for use again.

Electrodes with polymer:

Check open hole, you could find:

- Air pocket near the open hole.
- Polymer polluted near the open hole.

In this case it means that **it is probably not the electrode suitable for the application** for which it is used. Contact support.

Slow, unstable or "almost" correct measures

A slow, unstable or non-perfect measurement is unlikely to depend on a failure. Very often it depends on lack of precautions. **Check:**

- Air bubbles in the membrane.
- Top-up cap must be opened to allow the flow of electrolyte and the communication.
- Temperature not stable.
- Dry or dirty membrane.
- Clogged porous septums.
- Stored in distilled water.

Influence of Temperature

Temperature changes pH value of the solution to be measured, so it changes also the slope of the electrode. This variation can be offset by activating automatic compensation (with ATC).
Temperature moves the isothermal point of the electrode.
This variation can be compensated by calibrating with buffer solutions at the same temperature of the samples to be measured. Temperature influences the response time of an electrode too.

How to clean and store

- After measurements, **wash electrode with distilled water and neutral soap, and dry it with paper without rubbing.**
- Preserve in **storage solution**, never in water.
- In case the **porous septums** were **dirty**:
  Pepsin cleaning solution - removes proteins.
  Thiurea cleaning solution - removes metals.
- **Dirty membrane**: 30 seconds in HF solution.

If electrode is stored in water rather than in storage, it becomes unusable within a few weeks.

Advice to keep in mind

- Always fresh **buffer solutions**.
- **Top-up cap** open in measure and calibration.
- **Never store in water,** especially distilled water.
- **Temperature** plays a basic role.
- **Connection cables** are not eternal.
- Check **electrolyte** level (electrodes with filling).

In any case, pH measurements in laboratory with accuracy better than 0.05 pH are very difficult to obtain.

Quick guide to EC measurement problems

Measuring EC correctly hides many pitfalls.
In those few pages we will have a look on which are control procedures to define the reasons for possible malfunctions in the EC chain.

EC measurement chain

EC-meter

Conductivity cell

Buffer solutions

Critical points

Buffer solutions: if expired or polluted, they can prejudice the whole chain.
Connectors: in a moist environment they can oxidize.
Cable: assimilate moisture - subject to strong stress from use.
Conductivity cell: explained in detail below.

Life of a conductivity cell

Unlike pH electrodes, if a conductivity cell is not used, it does not become exhausted but "falls asleep" and slows down the measurement rate. To wake it up, immerse it in denatured alcohol for a minimum of 30 seconds or a maximum of 15 minutes.
Average life of a properly used conductivity cell is 24 months.
High temperatures, moisture, inside focused dirt and improper cleaning can shorten life of a conductivity cell even for many months.
Cable and buffer solutions also incline to deteriorate.

Operation

Conductivity is defined as the ability of ions contained in a solution to conduct an electric current.
It gives us a quick and reliable indication of the number of ions in a solution.
Conductivity is the inverse of resistivity. It does not give us a selective indication of the ions present in the solution (we measure all the salts present in a solution).
We categorize conductivity cells according to their cell constant:

0.1 = low conductivity (0 … 300 µS)

1 = standard conductivity (300 … 3000 µS)

10 = high conductivity (3 mS … f.s.)

The cell constant is the area described by the electrodes/plates (in square meters). The ratio of length to area of the plates is geometrically predetermined. This factor is called the cell constant.
With **cell constant = 0.1** you can calibrate the chain on one point between **84 µS or 147 µS**.
With **cell constant = 1** you can calibrate the chain on two points **1413 µS and 12880 µS**.
With **cell constant = 10** you can calibrate the chain on one point between **12.88 mS or 111.8 mS**.

Influence of Temperature

The conductivity of a solution is highly dependent on temperature and increases with increasing temperature. This increase is generally expressed in % / C° and is called the temperature coefficient (TC). If TC is applied, then the reference temperature (TR) must be specified: the two most common temperatures used in analytical workers are 20°C and 25°C.

Conductivity cell malfunction

The most common problems that can be found by measuring conductivity are:

- Measurements too low compared to the value sought.
- Unstable and completely out-of-range measurements.
- Temperature sensor inside the cell not measuring correctly.

The problems mentioned above, and many others, can be caused (and solved) by the following reasons:

- Air bubbles between the sensor and the outer glass/plastic protection.
  To make them disappear, shake the sensor or use a stirrer while calibrating and measuring.
- Cell immersed in too low buffer solution or too low sample.
  The level of the buffer solution or sample should reach about half of the conductivity cell.
- Sensor and plates/electrodes very dirty.
  Use only water and/or denatured alcohol to clean the conductivity cell. Do not manually clean inside the glass/plastic protection with paper or anything else because the platinum black covering the plates/electrodes may peel off.
- The conductivity cell is slow and detects measurements that are too low.
  The conductivity cell is lightly asleep and needs to be washed with denatured alcohol.

How to clean and store

- After measurements, **wash the conductivity cell with distilled water and dry it with paper without rubbing.**
- It can be stored dry, without any storage solution (no water storing).
- In case of heavily dirty sensor and plates/eletrodes, clean only with denatured alcohol.