Troubleshooting guide for pH electrodes

DO YOU WANT TO SAVE TIME & MONEY?

In this white paper you will find some tests you can do before unnecessarily buying a new pH electrode or sending an instrument without real need to service for repair.

Just click on the info you need

How to test your pH electrode

HAVING A PROBLEM RECALIBRATING YOUR PH METER?

Sensors dislike

How to store the electrode

How to clean your electrode

If you see a zero point shift –a reduced slope –long response time

Key questions to determine the correct pH buffer

- Frequency of use of the pH buffers?
- Reference temperature of the buffer?
- Color coding?
- Meter calibration settings pH value – Temperature value!

How to test your pH electrode

DO YOU HAVE A PROBLEM RECALIBRATING YOUR PH METER?

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pH measurements seem a very easy application, but be aware:
A lot of things can influence the result of your measurement.

The environment, the sample, the electrode, the cable, the meter, the buffers, the user.

The following pages will guide you through some easy tests to control why your pH calibration does not work anymore, and gives advise for better results.

But first:

Check if your electrode is being stored correctly:

e.g., you can't have a correct measurement with a dry electrode membrane or a dried out reference system.

Also, check if the electrode is connected well!

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

How to test your pH electrode

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STEP 1: IS THE ELECTRODE THE CORRECT ONE FOR YOUR MEASUREMENTS?

Ask yourself:

What's the lifetime of your electrode?

How frequent do you use it?

- Continuously
- Few measurements a day, week, month?
- What is the temperature of your sample?
- What kind of matrix?
- What's the pH range you are measuring in? (acid error, alkali error)

Information:

The lifetime of an electrode can be from 1 minute to several years! It all depends on the type you use for your application.

Choosing the right electrode can save you a lot of money.

- Go to the selector guide on our website (VWR.com, keyword: pH electrode) if you are looking for the best electrode for your application
- Download the pH handbook on our electrochemistry landing page if you want to learn about all the differences.
- Or contact an Avantor specialist for more information

Download the pH handbook

Test the electrode | **Sensors dislike** | **Correct storage** | **Correct cleaning** | **Correct buffer**

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STEP 2. DIAPHRAGM OR REFERENCE JUNCTION OF AN ELECTRODE

Check:

- If there is an air bubble near the junction: Shake the electrode, bubbles inside the electrode are a must, otherwise electrodes will crack at significant temperature changes
- If the junction is clogged
- In the case of gel electrodes, don't store in demineralised water

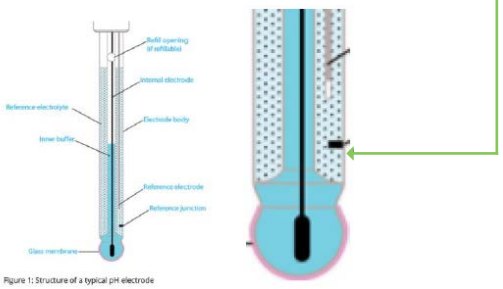

Figure 1: Structure of a typical pH electrode

Information:

The reference junction, also known as a diaphragm, creates electrical contact between the reference system and the sample solution.

Diffusion voltages at the junction are a common measurement error, so the junction plays a major role in the precision of measurements. To keep these potential disruptions small, the junction must guarantee a relatively large and consistent outflow of reference electrolyte. However, the junction must only be slightly permeable to prevent electrolyte from escaping too quickly, which is especially important with electrodes that use liquid electrolytes.

Different junction types have different outflow rates of electrolyte.

Gel electrodes have no outflow, but storing them in distilled water can disrupt the electrical contact because of diffusion of electrolyte out of the gel or polymer.

Download the pH handbook on this landing page if you want to learn about all the differences.

Download the pH handbook

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

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STEP 3: ELECTROLYTE LEVEL

Check:

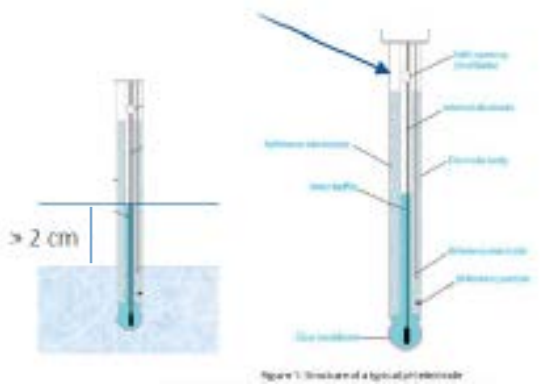
- Is the level of your inner electrolyte at least 2 cm above the level of your sample?
- Is the refill opening open during measurement? This avoids under pressure in the electrode as the electrolyte flows out
- Do you regularly rinse the electrode, change the inner electrolyte?

Information:

Law of communicating vessels: The electrode can be damaged if a sample enters the reference electrode.

Keeping the difference in level is good, means a good outflow, and less disturbance of the potential, giving more stable signals.

Download the pH handbook if you want to learn about all the different types of electrolyte and which one is best for your application



Download the pH handbook

Test the electrode | **Sensors dislike** | **Correct storage** | **Correct cleaning** | **Correct buffer**

How to test your pH electrode

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STEP 4: BUFFERS FOR CALIBRATION: ARE THEY FRESH?

Do you use:

- Fresh buffers for your calibration

Information:

- The value of a buffer can change when it is used too often, contamination by the electrodes, or by absorption of CO_2 from the air
- 7.00 buffers are especially sensitive (contamination by an electrode, as this is the optimum environment for bacteria or fungi to grow), while a 10.00 buffer is less stable because of the absorption of CO_2 from the air, causing the value to drop
- So change your buffer regularly. If you work with large bottles, always pour a small amount into a clean cup and close the bottle securely after use
- A solution to this problem is using single-use buffer bags or, if you have a large consumption, 'bag-in-boxes' with a flexible plastic container inside

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

How to test your pH electrode

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STEP 5: BUFFERS FOR CALIBRATION: WHICH ONE TO USE?

Do you use:

- The correct buffers for automatic calibration? The meter is programmed for certain buffer types. Also see the chapter on the correct buffer, pH/ temperature.

Information:

There are a lot of brands on the market that have different qualities and different values.

When using automatic calibration, check the ones that are programmed.

- DIN buffers: 1,679 - 4,006 - 6,865 - 9,180 - 12,454
- Technical buffers: 2,0 - 4,01 - 7,00 - 10,01

Different brands sometimes have different pH/ temperature behaviour.
Example: With pH 10,00 at 25 °C, buffer brand 1 can have a value of 10,52 at 5 °C while buffer brand 2 can have a value of 10,17 at 5 °C.

Check if your buffers have the same pH/ temperature behaviour as the supplier of the meter programmed in the automatic calibration.

You can always do a manual calibration, but this is riskier because your input needs to be correct.

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STEP 6: TEMPERATURE & PH: TEMPERATURE COMPENSATION

Check:

Is the temperature value on the meter's display correct?

If not:

- Enter the value manually and recalibrate
- Change the temperature probe*

If OK, go to step 7

Note: Temperature compensation only compensates for errors caused by altered properties of the pH electrode at other temperatures.

A sample measured at 60 °C has a different pH value when it is measured at 25 °C. This can not be predicted because every sample reacts differently (dissociation of molecules). It is not a measuring error. The effect is larger the further you get away from pH 7.

That is why you should always mention a pH value together with a temperature displayed next to it.

* An electrode with built-in sensor is easy to use, but more expensive to exchange. To save money you could use a pH electrode and a separate temperature sensor.

Information:

Temperature compensation is important for 2 reasons:

1) A pH electrode will behave differently when temperature changes.

It is made of glass, with internal, external liquids and junctions, which build up potentials that are influenced by the temperature. These changes are compensated by the meter, when using a temperature probe.

2) When calibrating, the values of pH buffers also change with temperature.

If the display does not show the correct temperature value, the calibration values will be translated by the meter incorrectly, giving an error.

Example: Calibrate at a temperature of 4 °C with buffers 7 and 10.

The real value of the buffer 10 at 4 °C is not really 10,00, but 10,52 (example) and 7,09 for buffer 7,00. If the meter does not know whether it is measuring at 4 °C and reads 25 °C, the values would be misinterpreted, giving an error or wrong results.

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

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STEP 7: MV READING

Check:

After cleaning (see section correct cleaning), connect the electrode to the meter and take buffer measurements in between rinsing the electrode and dip it dry.
(do not scrub as, this will cause an electric charge).

What is the mV reading of buffer 4 and 7 or 7 and 10?

Buffer 4:

Buffer 7:

Buffer 10:

Calculate the mV per pH unit: ……..

If lower than 56 mV/pH unit, replace the pH electrode.

Unstable reading, blocked diaphragm or deposits on membrane: Clean the membrane and diaphragm.

56 to 60 mV/pH (95% to 102%): Your electrode is working well. The problem might down to the meter: Do a reset and try again, if not OK contact our service department.

Information:

mV reading

The theoretical value of the slope is 59,16 mV per pH unit at 25 °C (Nernst).

For a pH measurement of buffers 4 and 7 the theoretical mV readings at 25 °C are:

pH 7,00: 0 mV

pH 4,00: 177,48 mV

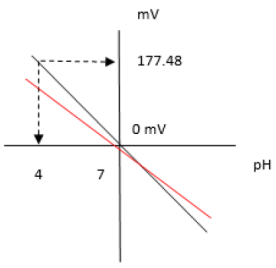
Per pH unit this is: (177,48 to 0): 3 = 59,16

With ageing, this value will become lower and accuracy will decrease.

Most meters will give an error when the value is less than 50 mV/pH unit.

Sometimes this value is expressed as % of theoretical value (59,16 at 25 °C)

$$u = u_0 + \frac{R \cdot T}{n \cdot F} \cdot \ln a_{Me+}$$



Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

How to test your pH electrode

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SUMMARY

If the results are not OK

- Try cleaning the electrode
- Rinse it with demineralised or distilled water
- For electrodes with liquid filling; replace the electrolyte
- Leave the electrode overnight in 3M KCl or other suitable product (depending on the electrode)
- Try again

If the results are OK

- The meter has caused the error
- Reset the meter
- Try to calibrate again
- If no change, contact your local Avantor service department

Tip: If you are stirring during calibration you should also stir during measurement!

Gentle stirring is advisable as it gives faster, stable results.

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

Sensors dislike

- The refilling opening being closed during measurement
- Dry storage or storing in distilled water
- Using the sensor as stirrer
- Repeated use of buffer
- Mechanical cleaning/rubbing of glass membrane
- Precipitation on glass membrane
- Diaphragm-polluted reference system

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

How to store electrodes

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STORAGE

pH combination electrodes and reference electrodes

- Do not store pH electrodes in demineralised or distilled water, certainly not a gel electrode
- As every reference electrolyte is an aqueous solution it has been found that the optimum storage liquid is the respective reference electrolyte of that combination electrode. The refill aperture has to be closed during storage time. Usually KCl 3 mol/L is used
- Gel filled combination electrodes have no refill aperture, so the drying out of its diaphragm has to be avoided at all cost. Therefore, gel filled combination electrodes must be stored wet in a 3 mol/L KCl solution or another suitable electrolyte. This also applies to polymer electrodes as well
- You need to store the electrode at room temperature: With higher temperatures your electrode will age faster
- After possible dry storage, the electrode has to be immersed for at least 24 hours to reform the swell layer in water or electrolyte solution. This can be done with KCl 3M

BDH Prolabo® KCl (3 mol/L) electrolyte solution

Cat. No. (100 ml) 83605.180

Cat. No. (500 ml) 83605.260

Storage bottle

Cat. No. 662-1248

Storage tube

Cat. No. 662-1167

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

How to clean your electrode

IF YOU SEE A ZERO POINT SHIFT OR A REDUCED SLOPE LONG RESPONSE TIME

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Clean your electrode.

- **The cleaning frequency:** Depends solely on the measuring solution, a cleaning time cycle has to be established individually for each pH measuring application
- **The cleaning interval:** This can vary between hours and weeks
- **The cleaning procedure** also depends on the kind of contamination
- **After cleaning,** always store for 12 to 24 hours in respective reference electrolyte and recalibrate

The following procedures have been found practical and effective

- Initially, always try to remove any deposits from the membrane or from the diaphragm by rinsing the electrode with a mild detergent
- Calcium deposits may be removed by soaking the electrode for several minutes in a solution of 0,1 mol/L HCl
- To remove oil and fat deposits the use of a strong household solvent is recommended. If this is unsuccessful a brief rinse in ethyl alcohol is advisable
- Measuring solutions containing proteins tend to contaminate the membrane and diaphragm of the electrode assembly. Soaking the electrode assembly for several hours in a solution of 1% pepsin in 0,1 mol/L HCl is normally a remedy (BDH Prolabo® Cat. No. (100 ml) 83603.180)
- An organic coating can be removed using commercially available glass cleaning solutions
- Measuring solutions containing sulphides will react with the silver chloride present in some reference electrolytes. This reaction will lead to the contamination of the diaphragm with silver sulphide deposits (black diaphragm). The electrode needs to be soaked in a thiourea/HCl solution until the diaphragm is totally bleached
- Highly resistant deposits may be removed with hydrogen peroxide or sodium hypo chloride
- Any other acid or alkaline soluble deposits may be removed by either rinsing the electrodes in 0,1 mol/L HCl or in 0,1 mol/L NaOH for a few minutes only

Under no circumstances clean mechanically i.e., with a knife, or sharp tool. Rubbing with a cloth will introduce static electricity into the glass shaft of the electrode and prolong the response time.

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

Key questions to determine the correct pH buffer

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HOW OFTEN DO USE PH BUFFERS?

Multiple times a day use:

- Bag-in-box packaging

Once a day or several times a week use:

- Bag-in-box
- Plastic bottle
- Dosing bottle

Only once in a while use:

- 30 ml buffer sachets for single use
- Dosing bottle

Download the brochure

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

Key questions to determine the correct pH buffer

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WHAT ABOUT THE REFERENCE TEMPERATURE OF THE BUFFER? 20 °C OR 25 °C

There are some companies which are accredited to produce primary buffer solutions.

One of these is Merck, another one is Hach (Radiometer).

In the DIN and NIST guidelines, 25 °C is the reference, but 20 °C is also possible.

In last century not all labs were temperature controlled, so they were warmer in the south and colder in northern areas.

Merck was one of the biggest companies in this field, and by referencing to 20 degrees, they differ from all the others.

But there is no advantage, just differentiation, and Merck uses both 20 and 25 degrees as referenced buffers.

DIN/NIST, as well as technical buffers, are secondary or tertiary buffers and reference to the primary buffer.

When referencing to NIST and DIN, the rest of the world outside of Merck references to 25 degree in the mean time.

Most of our buffer solutions are available in a 20 °C and 25 °C versions.

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

Key questions to determine the correct pH buffer

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DO YOU PREFER COLOUR CODING OR NOT?

Some of our buffer solutions are available in coloured versions:

This helps to avoid human errors during calibration.

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

Key questions to determine the correct pH buffer

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MOST IMPORTANT CHOICE: METER PH TEMPERATURE VALUE!

What are the values that are programmed in your meter?

An example:

Your buffers are stored at 10 °C: The programmed buffer is WTW. The used buffer is Merck.

Temperature	WTW	VWR	Merck
10	4,00	4,00	4,02
15	4,00	4,00	4,01
20	4,00	4,00	4,00
25	4,01	4,01	4,01
30	4,01	4,01	4,01
50	4,06	4,06	4,00

You calibrate your meter: Buffer 7 and buffer 10 at 10 °C: Real values at that temperature are: 7,05 and 10,11.

Temperature	WTW	VWR	Merck
10	7,06	7,04	7,05
15	7,04	7,02	7,02
20	7,02	7,00	7,00
25	7,00	6,99	6,98
30	6,99	6,98	6,98
50	6,97	6,96	6,95

The meters uses the programmed values at 10 °C 7,04 and 10,39 to adjust the system.

Temperature	WTW	VWR	Merck
10	10,39	10,11	10,11
15	10,26	10,05	10,05
20	10,13	10,00	10,00
25	10,00	9,94	9,94
30	9,87	9,89	9,89
50	9,35	9,74	9,74

At that temperature the pH value of buffer 10 gives you an error of 0,28.

Test the electrode | Sensors dislike | Correct storage | Correct cleaning | Correct buffer

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