Cleaning and maintenance of pH probes

Handling, storage and maintenance have a significant influence on the accuracy and life span of a pH probe. Even small things like air bubbles, crystallisation, low electrolyte filling, KCl leakage or contamination can have a negative effect. Avoid problems by doing the following:

1. Commissioning new electrodes

pH probes are supplied with a storage cap filled with internal electrolyte which is used inside the probe. This maintains the hydration of the glass bulb and the equilibrium inside and outside of the probe. The refill opening of refillable electrodes is also sealed with sticky tape to prevent liquid electrolytes from leaking during transport.
Tip: Condition a new electrode before it is used for the first time.

For refillable liquid electrolyte electrodes, first:
▶ Remove sticky tape (protective film) and/or cap over filling hole
▶ Fill with specified liquid electrolyte as required (up to approximately 3 mm below the refill opening)

Then, for electrodes using gel or liquid electrolyte:
▶ Check if the glass bulb contains any air bubbles. Remove any that are present by following the instructions in section 5.
▶ Condition according to manufacturer's instructions. This generally involves keeping the electrode in a sample or buffer solution for a few minutes. The response time of a new, conditioned electrode in pH buffers is usually less than 30 seconds at 25 °C.
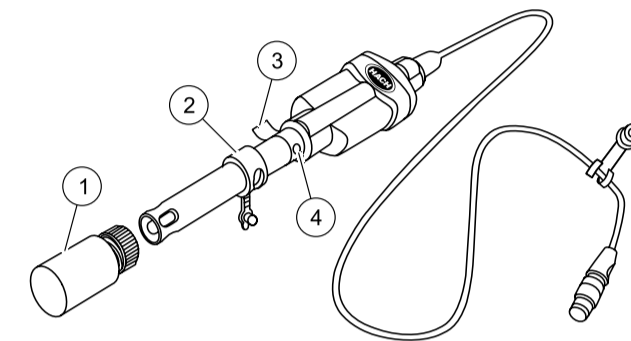

1 Storage container
2 Cover
3 Sticky tape
4 Refill opening

2. Liquid electrolyte electrodes

Refilling electrolyte
Refillable pH probes have an opening though which electrolyte can be poured. The fill level is dependent on the function. If there is sufficient electrolyte in the electrode (up to approximately 3 mm below the fill opening), hydrostatic pressure ensures there is a sufficient electrolyte flow through the diaphragm.

This also prevents the sample solution from penetrating the electrode. Leave some space below the refill opening so that KCl does not leak or crystallise. Open the refill opening before each measurement and close it if the electrode is no longer in use and is being stored.
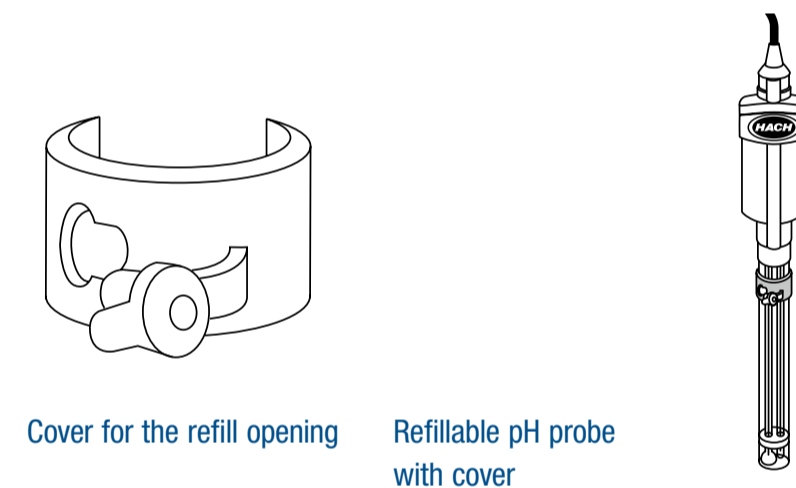

Cover for the refill opening   Refillable pH probe with cover

Removing electrolyte
If the internal electrolyte solution is contaminated, remove all of the liquid using a syringe with a cannula. Remove the liquid slowly and carefully to prevent damaging anything inside the electrode.

The correct refill solution is described in the electrode manual. The most used electrolyte solution is 3 M KCl; a variant is 3 M KCl saturated with AgCl.
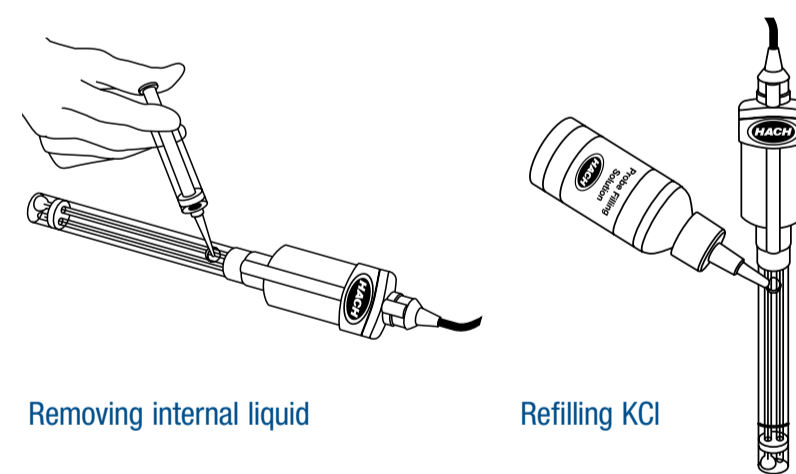
Removing internal liquid   Refilling KCl

Crystallisation
As a rule, crystallisation is neither damaging to the electrode nor affects its performance. External salt crystals can be removed by rinsing with water. Any salt crystals inside the electrode can be dissolved by immersing the electrode in warm (45 °C) water. Electrodes using saturated KCl should have visible crystals.

Formation of salt crystals on the diaphragm can be prevented by proper storage in a storage solution.

Innocuous crystallisation on storage cap, electrode shaft or refill opening   Rinsing the electrode

3. Regular maintenance

There are indications that the electrode requires cleaning:
▶ Long stabilisation times
▶ False or erroneous measurement values
▶ Loss of slope/sensitivity during calibration, less than 95 %

Careful maintenance ensures quick measurements, increases accuracy and extends the life span of an electrode. Regular maintenance of the electrode includes storing it in the recommended storage solution between measurements, as well as checking and replenishing the electrolyte filling. Optimal results will be achieved with the electrode if the diaphragm does not dry out.

An electrode must be regularly cleaned depending on the samples as bacteria, organic compounds and proteins will adhere to the probe surface over time. A good cleaning solution works selectively on the relevant contamination. This means greases, lubricants and oils are removed by non-ionic cleaning products or ethanol; proteins, such as those in food, are purged by an acidic pepsin solution and mineral deposits are dissolved by an acidic solution. Table 9 will help you to select the correct cleaning product.

Then rinse the electrode thoroughly with distilled water and store in the prescribed storage solution.
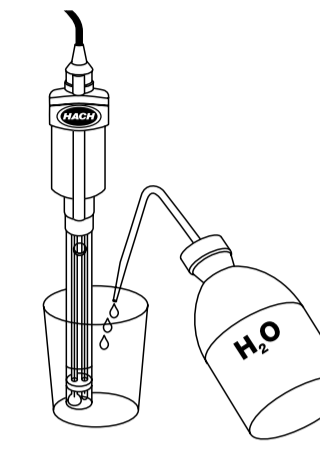
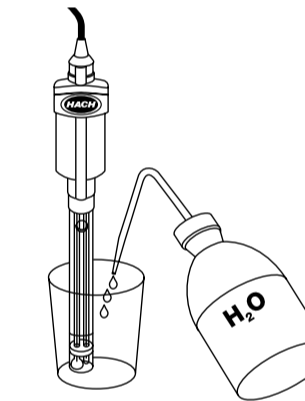Rinsing the electrode

Electrode cleaning solution

4. Regular cleaning of the pH glass bulb and diaphragm

For an optimum response time, it is necessary to remove impurities and deposits from the pH glass bulb and diaphragm. To clean the glass bulb, follow the instructions in the electrode manual. It is usually advisable to place the electrode in warm water or a special solution (see table 9) for a few minutes to keep the diaphragm permeable.
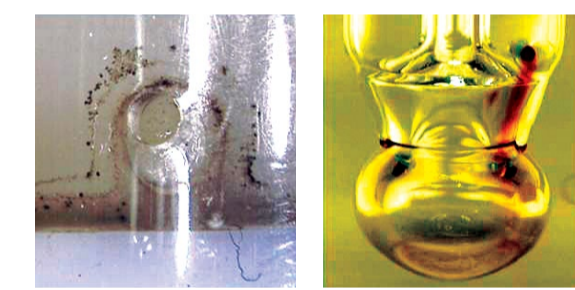
Contaminated reference junction   Correctly functioning ceramic diaphragm, effluence of electrolytes (red liquid)   Rinsing the electrode   Electrode cleaning solution
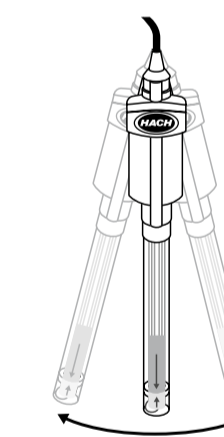
5. Air bubbles in glass bulb

The electrolyte in the electrode may move during transport or if it is stored horizontally. This may create air bubbles in the glass bulb that distort measurements or calibrations. Before every measurement, it is advisable to check that the glass bulb is sufficiently filled with electrolyte and no visible air bubbles are present.

If air bubbles are visible in the glass bulb, swing the probe in a circular motion several times till air bubble has been removed. Perform with no obstacles in vicinity. Please note: Gel filled electrodes may need to be replaced if a hole/air bubble is formed near to or around the diaphragm.
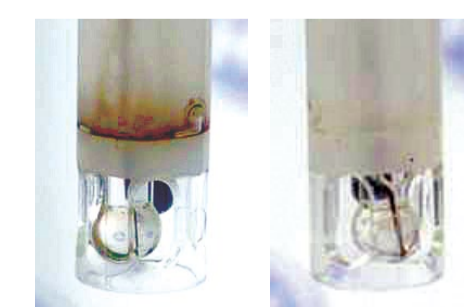

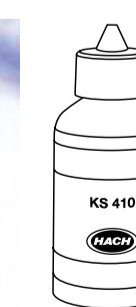Air in the glass bulb   Moving the electrode

6. Contamination inside the electrode

Some samples may penetrate the electrode via an open diaphragm and cause biological growth.
This contamination affects the performance of the electrode. Place the electrode in a thiourea solution for a few hours, then rinse thoroughly with distilled water.

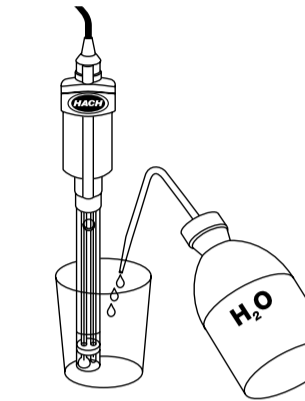Contaminated (left) and clean (right) gel electrolyte   KS410 thiourea solution

7. Contamination of the outer electrode

Contaminated samples or sample residue on the glass bulb may lead to erroneous results. Table 9 will help you to select the correct cleaning product. A contaminated glass bulb is usually cleaned in the following manner: Place the electrode in an electrode detergent solution for up to sixteen hours (overnight). Then rinse thoroughly with distilled water and place the electrode in a pH 4.0 buffer solution for a further twenty minutes.
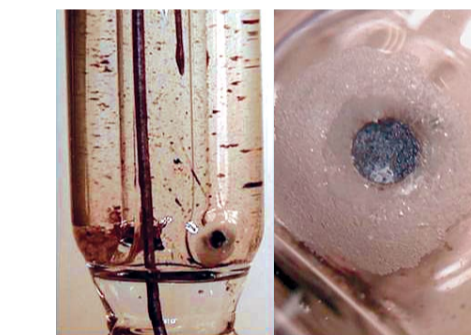

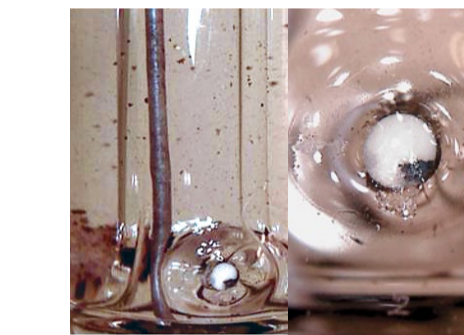Externally contaminated glass bulb   Rinsing the electrode   Electrode cleaning solution

8. Sulphide deposit

Sulphides and silver ions can form a dark deposit in refillable electrodes. This deposit may impair the operation of the diaphragm. Place the electrode in a thiourea solution for a few minutes to dissolve the deposit.

Ceramic diaphragm blocked by a sulphide deposit   Ceramic diaphragm after treatment with KS410 solution   KS410 thiourea solution

9. Selecting the correct cleaning product

Cleaning solutions for pH probes		Ethanol, acetone	Renovo N (alkaline solution of surfactants and polyphosphates)	Renovo X (sodium hypochlorite solution)	Electrode cleaning solution with phosphoric acid (10 %)	KS400 pepsin in HCl	KS410 thiourea solution	Buffer solution pH 1.09 (HCl) 40 °C
			250 mL	250 mL	500 mL	250 mL	250 mL	500 mL
Part number			S16M001	S16M002	2975149	C20C370	C20C380	S11M009
Contamination by sample	Surface water		5-20 min					
	Seawater			5-10 min				
	Wastewater			5-10 min		5-30 min	5-30 min	
	Activated sludge			5-10 min	5-20 min	5-30 min	5-30 min	
	Soil, sludge, clay		5-20 min		5-20 min			5-20 min
	Food and beverages			5-10 min		5-30 min	5-30 min	5-20 min
	Medical samples	5-10 min		5-10 min		5-30 min	5-30 min	
	Electroplating		5-20 min	5-10 min				5-20 min
	Paint, varnish, caustics	5-10 min	5-20 min					
	Cosmetics, soap	5-10 min	5-20 min					
	Petroleum products	5-10 min	5-20 min					
	Paper, cardboard		5-20 min	5-10 min				5-20 min
Type of contamination	General, light contamination		5-20 min	5-10 min				
	Inorganic, alkaline		5-20 min	5-10 min	5-20 min			5-20 min
	Organic	5-10 min		5-10 min				
	Proteins	5-10 min				5-30 min		
	Greases, oils	5-10 min	5-20 min					
	Sulphides		5-20 min				5-30 min	5-20 min
	KCl salt crystallisation		5-20 min					

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