Good practice for pH/ORP electrode users

pH

Endress+Hauser pH electrodes require proper conditions during storage, cleaning, and calibration to optimise the system performance and maximise electrode life.
Bad electrode practice can result in unreliable measurement.

This application note reviews the storage, rehydrating, chemical cleaning and reactivating of Endress+Hauser Memosens pH electrodes.

Storage

pH electrodes in general have a 6 month shelf life, then they can still operate in the process for the rest of their operating life.
Endress+Hauser pH electrodes are supplied hydrated, i.e. with a rubber cap filled with 3 mol/L KCL which keeps the membrane and diaphragm wetted and so ready for immediate use. It is important not to discard the rubber caps as they will be re-used for short-term storage after pre-calibrating the Memosens pH electrode in the future.
NOTE! Never allow the membrane and diaphragm to dry out! A short 10 minute period in air is unavoidable from time to time but must be kept to a minimum, if the electrode is hot then the allowable time is less.

Rehydrating

If the pH electrode dries out in the process or during storage, soak the electrode in 20°C 3mol/L KCL solution for 24 hours or 60°C 3mol/L KCL solution for 6hrs.
NOTE! There is a small chance that the pH electrode may not be recoverable.

Chemical cleaning

A coating on the pH electrode membrane (swell film) and diaphragm (reference junction) will impede the proper operation of the pH electrode and needs to be removed from time to time.

1. General Coating,
   - Rinse well with hot tap water and dry with a soft cloth.
   - Soak in 1.5 mol/L HCl (5%) for 15 minutes.
   - Rinse well with warm tap water and dry with a soft cloth.
   - Drain the reference electrode and refill with 3M KCL solution. (CPS41D only)
   - Soak the electrode in 3mol/L KCL solution for one hour* then calibrate.
2. Inorganic Coating,
   - Rinse well with hot tap water and dry with a soft cloth.
   - Soak in 0.1 mol/L tetrasodium EDTA solution for 15 minutes.
   - Rinse well with warm tap water and dry with a soft cloth.
   - Drain the reference electrode and refill with 3M KCL solution. (CPS41D only)
   - Soak the electrode in 3mol/L KCL solution for one hour* then calibrate.

Chemical cleaning (Continued)

3. Protein Coating,
   - Rinse well with hot tap water and dry with a soft cloth.
   - Soak in 5% HCl (or a mix of 0.1 mol/L HCl and 0.1% pepsin) for 15 minutes.
   - Rinse well with warm tap water and dry with a soft cloth.
   - Drain the reference electrode ⅄ and refill with 3M KCL solution. (CPS41D only)
   - Soak the electrode in 3mol/L KCL solution for one hour* then calibrate.
4. Silver Sulphide Coating
   - Rinse well with hot tap water and dry with a soft cloth.
   - Soak in 0.1 mol/L thiourea /1.5 mol/L HCl (5%) for 15 minutes.
   - Rinse well with warm tap water and dry with a soft cloth.
   - Drain the reference electrode ⅄ and refill with 3mol/L KCL solution. (CPS41D only)
   - Soak the electrode in 3mol/L KCL solution for one hour* then calibrate.
5. Grease and/or Oil Coating,
   - Rinse well with hot tap water and dry with a soft cloth.
   - Rinse with detergent or ethanol solution.
   - Rinse well with warm tap water and dry with a soft cloth.
   - Drain the reference electrode ⅄ and refill with 3mol/L KCL solution. (CPS41D only)
   - Soak the electrode in 3mol/L KCL solution for one hour* then calibrate.

   *Electrode response may be enhanced by substituting a mixture of 1:1 pH 4 buffer and 3M KCL solution for the soaking solution.
   ⅄ Note that in case of our gel electrodes replacing of the reference solution is not possible):

Note: Tougher deposits can be removed with hydrogen peroxide or sodium hypo-chlorite.

Reactivating

Reactivating the glass membrane (swell film)

Physical or chemical damage to the glass membrane may result in the pH electrode performing sluggishly. Reactivating the glass membrane may return the electrode performance.

1. Dip only the glass bulb of the pH electrode in a 10 % solution of ammonium bifluoride for 60 seconds, then immediately in 1:1 HCL: water for 10 seconds, this will neutralize the strong base.
2. Once this procedure is complete place the electrode in 3M KCL over night.
3. Recalibrate

ORP/REDOX (same thing)

Here is a quick check to determine whether your ORP electrode is responding correctly.

Take a reading of your tap water (this will typically be a value well below 200 mV) and then take a reading of the same tap water adding an equal volume of bleach.

In both tests you will need to allow the electrode to stabilise at a reading which may take up to 30 minutes. When the bleaches added you should get a much higher reading (up to 800 mV is possible through lower values, 300 to 600mV, are typical).

If the readings remain close to the readings for the tap water only, there is some problem with the ORP measurement system (i.e. the electrode sensing metal is dirty/coated or reference diaphragm is clogged). If your test of the bleach and water mixture gives the higher readings, the ORP measurement system is working.

ORP electrode Cleaning and Calibration Procedure.

Unlike pH electrodes, ORP electrodes require equilibration time after exposure to chemicals. Chemicals found in the cleaning and calibration solutions affect the redox potential on the metal surface resulting in an initial ORP offset.

Conditioning
Place a clean, pre-calibrated ORP electrode in process fluid (or tap water) to equilibrate before use.
Note ☞ The time needed for equilibration could vary from 6 to 12 hours.

1. Remove the dirty electrode from the process.
2. Install the conditioned ORP electrode.
3. Wash the dirty electrode with tap water.
   - Rinse with either a detergent, ethanol or acetone solution if fats or oil is on the electrode (Only if necessary)
   - Rinse with hypochlorous or hydrochloric acid if an organic coating is on the electrode (Only if necessary)
4. Rinse well with warm tap water and light mechanical cleaning using a green "kitchen sponge" and dry with a soft cloth.
5. Calibrate.
   Note ☞ Only use one value/type buffer solution for calibration and verification as mixing two different value/type buffer solutions will cause a reaction and block the diaphragm.
6. It will be necessary to leave the electrode in process fluid to equilibrate for anything from 6 to 12 hours.
7. The electrode is now ready for use.