



FAQ's on pH Sensors

1. What is the shelf life of a sensor?

The shelf life of a pH sensor depends on its storage conditions. Under the best of conditions, sensor may last well over twelve months on the shelf. The practical limit you should expect is six months to a year, when the sensor is properly stored. This does not mean that the sensor cannot be used after that date. For Glass electrodes and Flowing type reference and combination electrodes the shelf life does not have much impact on the performance. For diffusion type sensors (gel filled, non- flow) the wet pocket may be dried out during storage. This may result in evaporation of the water inside the sensor causing high impedance of the reference cell. Often it is sufficient to check the wet-pocket. If it is not completely dry, then refilling is all that is necessary to keep them on the shelf for another year.

2. Can a reference sensor be stored in demi-water?

Absolutely not ! Proper working of the reference-electrode is based on a highly conductive liquid junction (diaphragm). This requires a high salt concentration in this junction : the same high concentration as inside the electrode. Each sensor shows diffusion: salt ions flow from high concentration to low concentration. If the sensor is stored in demi-water, then the salt will diffuse from the electrode to the demi-water and therefore the sensor ages already during storage. The impedance of the junction will increase during this storage due to the diffusion process. That is why the sensor should always be stored in a storage solution that has the same salt concentration as the internal electrolyte. Only then there will be no diffusion effect during storage.

3. What is an ORP or Redox measurement?

ORP stands for Oxidation-Reduction Potential. Redox stands for Reductor / Oxidator. An ORP measurement is a potential measurement of the oxidizing/reducing power of a liquid. The equilibrium of reversible redox reactions is measured.

4. What is a rH measurement?

Put simply it is a calculated value which gives a measure of oxidizing (or reducing) power of a solution independent of the pH of that solution. Normal ORP is heavily dependent on the pH of the solution as well as the ability of the solution to oxidize or reduce. rH is the negative logarithm of the partial pressure of Hydrogen in water. It has been defined by Clark to identify the oxidation power of water that is treated with an oxidiser (such as Chlorine) or a reducer (such as Sulphite). The rH concept comes from the NERNST equation for pH measurement. $E = + RT/2F \ln [H^+]^2 / p[H_2]$ (the redox reaction is $H_2 \rightarrow 2 H^+ + 2e^-$). This is the real pH standard method and it is used to define the real pH value using the Hydrogen electrode. The theoretical zero mV value is defined as the output of a Platinum electrode in a solution with $[H^+] = 1$ and $p[H_2] = 1$ so when pure Hydrogen is used to saturate a 1 mol/l HCl solution, then the output of the Platinum electrode is zero mV. This Hydrogen electrode is used as primary standard by all meteorological institutes to calibrate pH buffer solutions. The output of a Platinum electrode in a water based solution, where the pH 1 and the $p[H_2]$ are not equal to 1, can then be described as $E = 59.16 (2. pH - rH)$, so if the pH is known (by measuring the water with a Glass electrode) and the output voltage of the Platinum electrode is known, then the rH is known as well. The scale goes from 0 (Hydrogen gas gives $p[H_2] = 1$, so $rH = 0$) to 42 which corresponds with Oxygen gas. The value of rH analysis is that the standard Redox potential varies with pH as well as with concentration of oxidant or reducing reagent. The rH value only changes when the concentration of oxidising reagent changes: so the user gets with rH analysis a pH compensated Chlorine analyser, when he wants to control Chlorine concentration.

5. The pH is measured at the so-called gel-layer of the glass electrode. Is it possible to remove / wipe off the gel-layer?

No, you cannot wipe off the gel-layer and with it the sensitivity of the electrode. The gel-layer is a chemically bound boundary that is formed when the pH-glass is emerged in (water based) liquid. This layer cannot be removed 'mechanically'. That doesn't mean that it is recommendable to clean the pH-electrode with for example a towel or paper tissue. Only by drying out (for a longer period not in the process or liquid or when the sensor comes in contact with hydroscopic fluids) or by etching with a fluoric acid - solution the gel-layer will disappear. The gel-layer will form again when the glass electrode is emerged into 'normal' water again.

But the gel-layer can be chemically attacked : contact with a hot Sodium hydroxide-solution will decrease the sensitivity of the glass-electrode almost down to zero. The explanation for this is that the gel-layer is then saturated with Sodium-ions (Na^+) instead of hydronium ions (H_3O^+). In this case again the gel-layer will be formed spontaneously when emerged into water with a less caustic pH-value.

6. What is the best way to clean a pH sensor?

First consider the dirt you are trying to clean off. Where does it dissolve in ? What will chemically attack it ? Next consider the sensor. What cleaner will have little or no effect on the sensor itself? Choose the solvent / soap / chemical that is the mildest and still removes the ' dirt'. Caustic is a risky choice; stronger concentrations will attack the glass at high temperatures. Dilute HCl is frequently a good choice. But again, the cleaner is chosen based on the dirt to be removed. The concentration of HCl should be as low as possible. 0.1 N is better than 1.0N. Consider about 4% or 1N to be a maximum. Always keep in mind that the mildest cleaner is the best cleaner. Organic coatings like grease or oil is best removed with a detergent such as dishwashing fluid. Organic solvent like Toluene will clean all right, but these are a-polar solutions. They will insulate the measuring membrane, so they should be avoided. If they are used, then detergent or polar solvents like acetone or alcohol must be used afterwards to remove the solvent from the membrane.

7. What is the application for the FU20 pH sensor with flat surface membrane?

The flat surface membrane reduces the risk of breaking the pH membrane by mechanical forces. This makes this sensor especially suitable for measurement in slurries. The standard membrane is protected for breakage by the fingers, but in some applications these fingers entrap dirt from the process. In normal one-phase process fluids the exposed pH membrane is a good method to utilise the self-cleaning effect of a fast flowing sample. In those applications the flat membrane tends to get coated more easily than the standard membrane. The chemical resistance of the flat membrane is less than that of the normal FU20, so for high temperature applications the flat membrane version is less suitable.

8. What is the ASymmetry POTential of a sensor?

The ASPOT is the mV offset at the isothermal point of intersection of the sensor. For most of our sensors the Isopotential point is 7 pH, 0 mV under ideal conditions. The ideal condition is that the reference systems in both measuring and reference cell are identical (symmetrical). If the mV output of the sensor is not 0 mV, then the cells are not symmetrical, therefore we call the offset Asymmetry Potential. The ASPOT mostly indicates condition of reference electrode. Possible causes of shift: depletion of potassium chloride and poisoning of reference electrolyte. If the ASPOT is higher than 30-40 mV the electrode needs to be replaced. There is one example where 40 mV Asymmetry potential is quite good. If you combine a Glass electrode with a reference system of 1 mol/l KCl (SM21-AG4) with a Reference electrode with saturated KCl (SR20-AC22), then the asymmetry of the reference cells is already 30 mV under ideal conditions.

When a pH sensor is calibrated with only one buffer solution or when a grab sample calibration is performed, the Asymmetry Potential is calculated and stored in the memory of the analyser.



9. What is the SLOPE of a sensor?

The slope of a sensor expresses how the sensor reacts on pH changes. Therefore other names for Slope are Efficiency or Sensitivity of the sensor. An ideal electrode couple has a mV change of 59.16 mV per pH at 25 °C. When calibrating the slope you need 2 buffers to characterise a line. When the calibration is completed, the Asymmetry Potential and the Slope are calculated and stored in the memory of the analyser. The slope of a sensor is expressed in % of ideal mV/pH value (59.16 mV/pH is 100% @ 25°C) and mostly indicates the condition of the glass electrode. Possible causes of decrease: Wrong or old buffer solutions, coated pH membrane, calibration before the measurement has stabilized, plugged liquid junction. If the slope lower than 70% the electrode or higher than 110%, the analyser will give a FAIL message indicating a real bad condition of the sensor. A good pH sensor has a Slope between 95 and 100%.

10. What is the ITP of a sensor?

ITP stands for Isothermal Point of intersection, also called so-potential point. When we plot the mV values against the pH value for a pH sensor at different temperatures, then all these lines have one common point: the iso-potential point. Ideally this point is at 7 pH, 0 mV. Most Yokogawa pH sensors have “Symmetrical Reference Systems” with a pH value of the internal electrolyte solution of 7.00. The mV output of the sensor is according to Nernst: $E = E_0 - 59.16 \times (T/298) \times (\text{pH} - 7.00)$.

11. When would I want to calibrate one point, two points or three points?

After long exposures to high temperatures the internal pH value may drift and the ITP will shift accordingly. It is possible to calibrate the ITP, if calibration is done at 2 different temperatures. For normal industrial applications this third calibration is unnecessary. Basically there are three methods for calibration: a) Grab sample calibration (process calibration) or single point calibration, b) Two-point calibration (buffer calibration), c) Three-point calibration.

a) One point calibration

Only the ZERO (offset) is adjusted and the Slope is kept at 100% (or previously calibrated value). This method gives a reasonable accuracy and is done mostly by comparing the on-line pH with laboratory readings of a grab sample.

b) Two point calibration

The two-point calibration method is the preferred method. Two buffer solutions with a different pH value adjust both ZERO (offset) and SLOPE of the sensor and the ITP is kept at 7.00 pH (or previously calibrated or programmed value). One buffer solution (A) will have a pH value equal to the pH value of the ITP. The second solution (B) should have a pH value close to the pH value of the process. Normally value of pH 4 for acid samples, pH 9 for alkali samples. This is most common calibration procedure: easy, fast and accurate.

c) Three-point calibration

The three-point calibration does not require three buffer solutions, but it requires calibration at 2 different temperatures. First the ZERO and SLOPE are determined by normal buffer calibration at standard reference temperature. Then the buffer solution with a pH value different from the ITP value is warmed up and the intersection with the previously calibrated standard temperature line is calculated.

Microprocessor instruments have Automatic Buffer Recognition. Make sure the buffer solutions are stored into memory. Typically the NIST buffer solution for the 4 is 4.01, 7 is 6.86 and 9 is 9.18 pH. A stability check may be included to have a bigger accuracy.

12. How often do I need to calibrate my pH system?

Frequency of calibration is highly dependant on the type of application: temperature, pressure, abrasives, harsh chemicals etc. etc. and the customers requirements for accuracy. Many process pH customers do a single point grab sample calibration frequently and a two point calibration less frequently.

Frequent adjustment normally indicates a bad performance of the analyzer. The more customers adjust the analyzer, the higher the measuring error they will experience. A good pH analyzer does not require more frequent adjustment than once per month. Don't confuse calibration and maintenance e.g.: good calibration but bad cleaning.

13. Do I need to re-calibrate after cleaning my pH-electrode?

If the pH analyzer gives an error due to fouling, then it is sufficient to clean the sensor and it is not necessary to recalibrate the sensor. If the pH analyzer has been calibrated with a coated sensor, then you have fixed the fouling error by offsetting the calibration values. Then you must recalibrate the sensor after you cleaned it, because a fouled sensor has a different ASY a Slope than a clean sensor.

At some (especially fouling) applications the pH-electrode has to be cleaned more regularly then normal, automatically or not. Re-calibration is not necessary. Checking the accuracy with a standard solution without calibration will suffice.

14. What gives me an indication of the fouling or poisoning of the sensor?

The logbook function will identify the condition of the sensor. If the Asymmetry potential or the Slope show irregular and inconsistent values, then this often indicate a fouled sensor. On-line the impedance monitoring function indicates the condition of the sensor: especially the reference element.

The impedance measured on-line is a valuable indication of the condition of the electrodes. The measuring electrode has an impedance in the Mohms range. A new reference electrode has an impedance of 1-5 Kohm, measured in a calibration buffer. In applications like demineralized water the measured impedance value is normally higher than 100 Kohm. Increasing impedance values are a good indication for fouling or poisoning of the sensor.

If the sensor is fouled, then cleaning is required. When the sensor is poisoned it has to be replaced.

A flowing-type or refillable type electrode can be applied if fouling or poisoning often occurs.

15. What advantage does the dual amplifier system give?

Excellent noise rejection, common mode and serial mode noise are both minimised by this design. If this sounds like technocrap to you, I sympathise. In plain English it means that normal pH meters are grounded in two ways: with a grounding wire to the power outlet or safety ground and via the reference electrode to the process fluid. Industrial plants are famous for having dirty grounds causing stray currents and so called ground loop currents. These groundloop currents find a good conductor in the reference electrode and make this electrode part of the current loop. Ohm's law says that this groundloop current develops a voltage drop over the junction (diaphragm) of the electrode = measuring error. Finally the current will electrolytically destroy the little battery: the reference element (Silver/Silver chloride). The possibility of earth loops via damp and damaged cables is also minimised. This feature is of particular importance when measuring in low conductivity waters such as in power station applications; in applications where the process is contained in insulating materials (Fibreglas vessels are infamous) and in applications where high currents / voltages are applied. The solution ground works as a lightning arrestor for ground loop currents!

16. What is the temperature effect on pH glass-resistance?

As a general rule, the glass-resistance will increase by 100 % with every temperature decrease of 10°C. Likewise the glass-resistance will decrease by 50 % with every temperature increase of 10°C.

The impedance reported in our specifications and text plates are the impedance values at reference temperature, which is 25 °C or the lowest specified working temperature if this is higher than 25°C

17. What does the temperature compensation when measuring pH?

a) temperature compensation of the sensor characteristics : pH is a potential measurement with a measuring electrode of (mostly) pH- sensitive glass. A pH-amplifier transforms the electrode potential into a pH-value. This is done by the known rule between the potential and the pH of the liquid : Nernst's Law. According to Nernst's law the sensitivity of the glass electrode will change proportional with the measuring temperature in ° K. : $E = E_0 + (R \times T / F)$. If the temperature is higher the potential change will be higher per pH or less at lower temperatures. For example : at 50°C the electrodes sensitivity is 64.12 mV per pH, at 25 °C the sensitivity is 59.16 mV/pH.

The temperature compensation compensates for this change per pH. Because of this the exact pH-value can be calculated at different temperatures.

b) Temperature compensation of the process value. Done with TC settings or with NEN

18. Can a cable of the PH20 or FU20 be shortened?

Basically not. A good pH cable is a coaxial low noise cable, because pH measurement is measuring very low voltages at a high impedance.

FAQ's taken from: http://www.yokogawa-europe.com/products_Ai_FAQs_1.htm#1-1