pH Sensors and Electrodes
"Maintaining your Yokogawa pH Monitoring System"

Why Is Sensor Maintenance Required?

When a quality pH sensor system is undamaged, cleaned and properly calibrated it will provide a measurement that is accurate and reliable. Even if an electrode is in a process that does not cause coating, plugging, abrasion or other problems, it still must be calibrated periodically to correct for aging of the sensors and the non-recoverable changes to the electrodes that take place.

These effects of aging usually happen slowly therefore, calibration should not be necessary more frequently than about once a month. If more frequent calibration is called for, it is usually because (1) the process is aggressive; (2) the electrode cleaning process used was not effective; (3) the routine calibration was not properly executed; (4) the pH readings are temperature dependent or (5) the wrong electrodes have been selected.

Users desire an accurate, reliable measurement with a reasonable electrode life while minimizing the frequency or complexity of maintenance that is needed. However, ensuring the electrodes are clean and calibrated will always involve some amount of maintenance.

The measurement results obtained from dirty or faulty electrodes can be anything from slow response, to a completely erroneous reading.

Therefore, the accuracy of the pH measurement is directly dependant upon the frequency of maintenance, and the maintenance frequency (and also the method used) is directly dependent upon the importance and/or aggressiveness of the process.

> ***NOTE***
> *The following periodic maintenance advice is intentionally general in nature because pH sensor maintenance is highly application specific.*

General Maintenance Procedure

The basic maintenance procedure for pH sensors/electrodes includes: (1) **Check** to see if electrodes need to be cleaned; (2) **Cleaning** the electrodes properly, then (3) **Re-checking** to see if the cleaning was effective and finally, (4) **Calibrating** the electrodes when it is necessary.

Checking and Cleaning the pH Electrodes

All pH electrodes should be cleaned on a periodic basis. The frequency of this cleaning is dependant upon the severity of the process (potential for coating or fouling) the electrodes are exposed to. An easy way to determine if the electrodes need to be cleaned is to, remove them from the process and wash them off with either DI or Tap water. Place the electrodes in a pH 4.01 buffer. If the displayed value is within 0.10 pH of the buffer value, the electrodes can be considered clean. Put the system back on-line.

***Checking**:* To determine if the electrodes need cleaning, remove them from the process and rinse them off with either DI or Tap water. Place the electrodes in a pH 4.01 buffer and allow the reading to stabilize. If the displayed value is within **0.10 pH** of the buffer value, the electrodes can be considered clean and the system can be placed back on-line. If the displayed value is outside the 0.10 tolerance, the electrodes should be cleaned.

Cleaning: A variety of cleaning solutions can be used depending on the coating effects of the process on the electrodes. Typically a 5 to 10% solution of HCl (or Muriatic) works well.

1.) First, rinse off the electrodes/sensor in just plane water to remove any heavy process coating using a soft brush, taking care not to damage the electrodes.

2.) Immerse the electrodes in the cleaning solution for 1-2 minutes, agitating them regularly. The pH reading will drop below 1.00 pH. Use the soft brush to clean off any remaining coating deposits.

3.) Once the reading has stabilized, remove the electrodes from the acid and rinse them thoroughly with clean water to avoid contaminating the buffer solution used in the next step. The pH of the rinse water should be close to pH 7.

pH glass is a porous glass and retains some of the last solution in which it was immersed. When you place the electrodes in the rinse water you may notice the pH reading settle out between pH 3 or 4. This means there was still some acid in the pH glass. After the reading has stabilized, wash the electrodes again in fresh rinse water. The pH will again climb and may settle out between pH 5 or 6. If so, some cleaning acid may still remain. wash the electrodes again, or until the final reading is close to pH 7.

4.) Place the electrodes back in the pH 4 buffer solution. If the displayed value is within **0.10 pH** of the buffer value, the electrodes are clean and do not require calibration. Put the system back on line.

If the value is outside the tolerance (0.01 pH), then a two point buffer **calibration** is require.

NOTE

EXA mains powered instruments allow users to do "on-line" cleaning of the pH electrodes and automatically check if the cleaning was effective. This capability can eliminate the manual "Check" step for the user.

Calibrate: A pH measurement loop requires regular calibration of the electrodes to compensate for their normal aging and also deterioration caused by the process. Typically this is done about once a month. Always use fresh buffer solutions to avoid the possibility of introducing errors from contaminated or aged solutions. Buffers supplied as liquids have a limited shelf life, especially alkaline buffers, which can absorb $C0_2$ from the air. Yokogawa strongly recommends NIST (primary) buffer standards in order to ensure the best accuracy and best buffer capacity is available.

1.) Rinse the electrodes thoroughly with clean water to remove any remaining cleaning solution. Then, immerse the electrodes in the first buffer solution (usually the neutral 6.87pH buffer) and let the measurement stabilize.

2.) Adjust the meter reading to the pH value of the buffer solution according to the method selected (automatic or manual).

3.) Rinse the electrodes with clean water to remove the traces of the first buffer. Then, immerse the electrodes in the second buffer solution usually 4.01 or 9.18 depending on the measuring range) and let the measurement stabilize.

4.) Adjust the meter reading to the pH value of the buffer solution according to the method selected (automatic or manual). A check for correct calibration can now be done by immersing the sensor again in the first buffer solution (after rinsing) to see if the reading is accurate. If it is not, the calibration should be repeated.

WARNING

During buffering the liquid earth and the temperature compensator must be Connected and the buffer solution temperature must be within the technical specification limits as indicated on the type plate.

Calibration

There are two commonly used methods of calibration; Automatic and Manual. Both achieve the desire results of adjusting for the aging (diminishing accuracy) of the electrodes. Users should choose the method which best suits their maintenance requirements and capabilities.

Automatic Calibration

EXA instruments offer internally programmed buffer tables, to calculate the buffer value at the actual temperature during the calibration. In addition, the stability of the reading is automatically calculated and when the reading has stabilized fully, automatic adjustments of slope and asymmetry values are made. A menu driven system prompts the operator through a simple, foolproof routine.

Manual Calibration

EXA also offers this method, where the operator decides the actual pH value to enter. Manual calibration is most often used for single-point adjustment of the asymmetry potential, by comparison method (grab sample). Manual calibration can also be used to perform a full 2-

point calibration with solutions other than the NIST buffers that are listed in the calibration tables. In this case, the solutions are applied sequentially as in the AUTOCAL method, but the user determines the adjustment of reading and stability.

A Third Alternative

Yokogawa pH Analyzers offer a third means for calibration called **Sample Calibration**. This function allows users to input. The operator activates the "SAMPLE" calibration routine, at the same time as taking a representative process sample. After determining the pH of this sample by independent methods, (in the Lab for example) the reading can be adjusted. While the sample is being analyzed, EXA holds the sample data in memory, while continuing to control and read pH normally.

Note

During manual calibration the temperature coefficient remains active and all readings are referred to 25 °C. This makes grab sample calibration easy and accurate. However, if the manual calibration technique is used for buffer calibration, the temperature coefficient must be set to zero in maintenance mode in the "TEMP" routine.

CALIBRATION PARAMETERS

Asymmetry Potential

The Asymmetry Potential **(*AS*)** also referred to as the millivolt offset, is an indication of the condition of the **reference electrode**. When the millivolt offset is greater than +/-30mV from zero, it is advisable to consider replacing the reference electrode. However, the correction limits of the EXA pH analyzers are up to +/-120mV. Outside this range an **E2** error message will appear on the second line display.

Slope

The Slope **(*SL*)** also referred to, as the efficiency of the electrode, is an indication of the condition of the **measuring (glass) electrode**. The slope is displayed in a percentage (%) value, with 100% SL being ideal. The factory default values are 70% - 110% of theoretical and are user programmable from the Service level. When the calculated slope exceeds the programmed values, an **E3** error message will appear on the second line display.

Reference Impedance

The Reference Impedance **(*RZ*)** also referred to, as the resistance of the **reference junction**, is an indication of a precipitate (blockage) forming at the reference junction and the electrode needs cleaning. This resistance is also influenced by the conductivity of the process solution. Typically a clean reference junction will have a resistance of less then 10-15k Ohms, but in low conductivity solutions, RZ values between 200 and 500 K Ohms are not uncommon. When the RZ value starts to approach 30 -35 K Ohms, the electrode will start to have a slow upward drift. When the reference impedance exceeds 100 K Ohms an **E6** error message will appear on the second line display. The RZ value is user programmable between 50 - 999 K Ohms from the Service level.

Buffers Solutions: Refer to **Technical Note TNA0917 "A Word About Buffers"** for more information.