Care and Maintenance of pH Electrodes in High Purity Water Applications

Introduction:

The information covered in this Technical Note describes the proper care and maintenance of the pH electrodes used in High Purity Water Applications. The electrodes (P/N SM21-AG4, SM60-T1, SR20-AC32), cables (P/N K1500FV, WU20-PCXX, for each electrode)and holder (P/N FF20-S33*B) have been selected to best address the problems common to high purity applications, such as:

Reference Junction Potentials: There is a large electrical potential created between the highly conductive KCl solution in the reference electrode and the low ionic process, causing a high impedance (resistance) across the reference junction. This increased junction potential causes a reference voltage offset and resultant measurement error. A Positive Pressure Reference (flowing) Electrode (Bellomatic) (P/N SR20-AC32) is required to solve this problem.

pH electrode response: A low impedance Glass Electrode (P/N SM21-AG4) is necessary to minimize slow response. Controlling the flow rate through the sensor holder (2 GPH or less) eliminates erratic measurement readings.

Surface static charges: A solution ground electrode (P/N K1500FV) is an integral part of all Yokogawa pH sensor assemblies. This electrode eliminates interference from ground loops that may exist in the process, and also any static charges (common to high purity measurements) that may build up on the measuring electrode.

Maintenance:

Diagnostics

The EXA PH202 and PH450 have built-in diagnostics to provide both “dynamic” and “routinely updated” data on the status of the proper functioning of the individual electrodes. The diagnostics include: AS -Asymmetry Potential (reference electrode offset); SL -Slope (pH electrode efficiency) both of which are updated after each two-point calibration. Also, the diagnostics for Z_1 and Z_2 – Impedance checking (resistance of the reference electrode junction) which are dynamic - continuously updated. Understanding the information provided by the diagnostics will help determine the type and frequency of maintenance that is required.

Cleaning

In order to achieve accurate, reliable measurements, care must be taken in the storage, cleaning and calibration of the measuring electrodes. For Pure Water applications, cleaning is not required as frequently and is usually accomplished at the same time routine calibration is done.

Cleaning is accomplished by immersing the electrodes in a 5-10% HCl solution for several minutes, then rinsing thoroughly in deionized water. Never wipe the pH electrode glass

membrane as you may damage it. If drying is necessary, blot the membrane surface with a clean, soft Kim-wipe or paper towel. The temperature sensor does not require any maintenance.

Calibration

Before electrodes are placed into initial service and periodically thereafter, they should be *cleaned* and *calibrated* using a two-point method. Two-point calibration corrects for changes in both the output of the pH measuring electrode (slope) and the millivolt offset (Eo) of the reference electrode, by comparing the measured values to those of known buffer solutions.

All EXA pH instrumentation has preprogrammed buffer tables that are accessed when the Auto Cal function is used. These pre-programmed tables include choices for both NBS (N.I.S.T.) buffers, which correspond to 6.86 pH, 4.01 pH and 9.18 pH at 25° C and NBS *traceable* or *technical grade* buffers, which are pure NBS buffers that have been adjusted to read 7.00, 4.00 and 10.00 respectively. If traceable buffers are used, and the default values in the preprogrammed Buffer Tables have not been changed, an error of .14 pH (7.00 - 6.86 = .14) will occur. To eliminate this situation, either use pure NBS buffers or select the correct Buffer Tables that match your buffers through the instrument software.

For further information regarding NBS vs NBS *Traceable* buffers, refer to the **Technical Note TNA0917 "A Word about...pH Buffers."** For information regarding the reprogramming of the EXA PH202 buffer tables, refer to section 5-3-3 (Code 24) in the instruction manual. For the reprogramming of the EXA PH450 refer to **"Technical Note TNA0905 "PH450 Analyzer Programming Custom Buffer Tables."**

EXA AUTO CAL NBS BUFFER TABLE

TEMPERATURE		pH Value		
°C	°F	pH7	pH4	pH9
0	32	6.98	4.00	9.46
5	41	6.95	4.00	9.40
10	50	6.92	4.00	9.33
15	59	6.90	4.00	9.28
20	68	6.88	4.00	9.23
25	77	6.86	4.01	9.18
30	86	6.85	4.02	9.14
35	95	6.84	4.02	9.10
40	104	6.84	4.04	9.07
45	113	6.83	4.05	9.04
50	122	6.83	4.06	9.01

TYPICAL NBS *TRACEABLE* BUFFER TABLE

TEMPERATURE		pH Value		
°C	°F	pH7	pH4	pH9
0	32	7.13	4.00	10.34
5	41	7.10	4.00	10.26
10	50	7.07	4.00	10.19
15	59	7.05	4.00	10.12
20	68	7.02	4.00	10.06
25	77	7.00	4.00	10.00
30	86	6.99	4.02	9.94
35	95	6.98	4.02	9.90
40	104	6.97	4.04	9.85
45	113	6.97	4.05	9.82
50	122	6.97	4.06	9.78

Calibration using the EXA PH450:

When performing a calibration, always start with fresh buffer solutions. You will need two buffers (preferably 7.00 and 4.00) and deionized water to rinse the electrodes.

1) Fill separate beakers with buffer solutions (7.00 and 4.00).
2) Clean the electrodes in 5-10% HCl solution as described above.

NOTE: For a detailed screen shot on how to perform an automatic calibration on the **EXA PH450** refer to **"Technical Note TNA0916 "PH450 Proper Calibration Procedure".**

3) Immerse the electrodes in the first buffer solution (7.00).
4) To perform Automatic Calibration, push the **wrench** (commissioning) icon on main screen.
5) Under the Execute title push the **diamond** next to **Calibration/Wash**.
6) Push the diamond next to **Automatic zero/slope** feature.
   In the dropdown box at the bottom of the screen, four different buffers can be select.
7) Select the one titled **Buffer 6.9**.
   The main display will start flashing and continue until the reading has stabilized. Once stabilized, the main display will lock onto the reading and store it in memory. The lower protion of the display will now ask you to either **Go to buffer 2** or **Calibration Complete**.
8) Press the **diamond** next to **Go to buffer 2** to select the second buffer of the two point calibration.
9) Remove electrodes from the 7.00 buffer and rinse it thoroughly in deionized water, then blot the electrodes to remove any excess water.
10) Immerse the electrode assembly in a sample cup of 4 buffer solution.
11) In the dropdown box, select the one titled **Buffer 4.0**.
    The main display will start flashing and continue until the reading has stabilized. Once stabilized, the main display will lock onto the reading and store it in memory.
12) Press the **diamond** next to **Calibration Complete** at the bottom of the screen.
    The instrument calculates the (Eo) reference electrode offset and the slope (efficiency) of the pH electrode.
13) A final screen will come up and at the bottom of the screen press the **diamond** next to **Accept Data.** The instrument recalculates the (Eo) reference electrode offset and the slope (efficiency) of the pH electrode and updates the stored calibration values and returns you to the original Calibration screen.
14) To return to normal measuring mode press the **House icon** at the top right of the screen.
15) Remove electrodes from the 4 buffer, rinse them in deionized water and put back online.

You can now read the diagnostics to ensure the electrodes are functioning properly.

1) From the Home screen press the **magnifying glass** icon.
2) At the bottom of this next screen press the **diamond** adjacent to **Next**.

The display will show you the zero mV output from the electrode (AS), Slope (SL) and Impedance 1 and Impedance 2. The two values you are interested in, are AS and SL. The (AS) asymmetry potential is ideally 0 mV and has a correction limit of ± 120 mV. When the asymmetry potential is greater than ± 60 mV, it will be slower to respond and needs to be replaced for this application.

Ideally your (SL) slope value should be 100% and its correction limits are 70% to 110%. When the slope drops to less than 85%, it indicates that the pH electrode has lost some of its efficiency (mV output) and will typically have a slow response. At this point it is recommended that the pH electrode be replaced.

Calibration using the EXA PH202:
When performing a calibration, always start with fresh buffer solutions. You will need two buffers (preferably 7.00 and 4.00) and deionized water to rinse the electrodes.

1) Fill separate beakers with buffer solutions (7.00 and 4.00).
2) Clean the electrodes in 5-10% HCl solution as described above.
3) Immerse the electrodes in the first buffer solution (7.00).
4) To perform Automatic Calibration, push the **mode** button on the front panel of the PH202.
5) The lower (2nd line) display will ask you **Auto Cal YES/NO**? Answer **YES**.
6) The main display will start flashing and continue until the reading has stabilized. Once stabilized, the main display will lock onto the reading and store it in memory. The lower display will now ask you **Cal End YES/NO**? Answer **NO**.
7) Remove electrodes from the 7.00 buffer and rinse it thoroughly in deionized water, then blot the electrodes to remove any excess water.
8) Immerse the electrode assembly in a sample cup of 4 buffer solution and allow it to stabilize.
9) The lower display is asking you **Cal 4 YES/NO**? When the reading is stable, press **Yes**. The main display will start flashing and continue until the reading has stabilized. Once stabilized, the main display will lock onto the reading and store it in memory.
10) The lower display will now ask you **Cal End YES/NO**? Answer **YES**.
11) The display will now flash **WAIT**. During this waiting period, the instrument recalculates the (Eo) reference electrode offset (asymmetry) and the slope (efficiency) of the pH electrode and updates the stored calibration values.
12) At the end of the waiting period the instrument will return to normal operation, or continue to **HOLD** the output if the Hold function is activated.
13) Remove electrodes from the 4 buffer, rinse them in deionized water and put back online.

You can now read the diagnostics to ensure that the electrodes are functioning properly.

1) Press the **mode** button. The lower display will ask **AUTO CAL YES/NO**? Answer **NO**.
   Then, **MAN CAL YES/NO**? Answer **NO**.
   Then, **DISPLAY YES/NO**? Answer **YES**.

You will now be able to scroll through the choices for your second line display by continually pressing the **NO**. [Your choices are: temperature , AS (asymmetry) , SL (slope), Z1 (impedance of measuring electrode), and Z2 (impedance of reference electrode)].

The two values you are interested in, are AS and SL. The (AS) asymmetry potential is ideally 0 mV and has a correction limit of ± 120 mV. When the asymmetry potential is greater than ± 60 mV, it will be slower to respond and needs to be replaced for this application.

The (SL) slope value should be 100% and its correction limits are 70% to 110%. When the slope drops to less than 85%, it indicates that the pH electrode has lost some of its efficiency (mV output) and will typically have a slow response. At this point it is recommended that the pH electrode be replaced.

Reference Electrode
There are three major causes for a high reference impedance: (1) low conductivity of the solution (which is the case for High Purity applications); (2) the flow rate past the reference

electrode is too fast not allowing electrochemical contact between the measuring electrode and the reference electrode; and (3) the reference junction fouling or plugging.

For high purity water applications, a flow rate of 2 GPH or less is recommended. A faster rate results in unstable readings.

If the impedance checking function of the EXA instrument is usually turned off for High Purity applications since the real cause for the increase impedance is the low conductivity of the water and not fouling as found in other applications. It this diagnostic is to be used, you need to determine the correct impedance default value by reading the Z2 diagnostic to see what the actual impedance value is for the process. It is typically 500K ohms. If it is higher, check to ensure the flow rate past the sensor is less than 2 GPH and that the grey stopper plug has been removed from the reference electrode.

Refilling the Bellomatic Reference Electrode
To refill the Bellomatic reference electrode:

1) Unscrew the cap from the top of the electrode and remove it. Be careful and the reference element is attached to this cap.
2) Take a pencil and with the eraser end facing down, insert it into the electrode and apply pressure to the bellows until they are compressed and hold in place as you insert the rubber stopper in the bottom of the electrode. This will hold the bellows in place.
3) Fill the electrode with electrolyte to just below the neck. Carefully screw the cap back with the reference elements on it back on the electrode. Whenever the electrode is in use, the rubber stopper must be removed.

Spare Parts
PH450A-G-U/UM (pH Analyzer)
FF20-S33*B (Flow Through Holder for stainless steel with ½" FNPT inlet and outlet)
SM21-AG4 (Shockproof pH Electrode)
SR20-AC32 (Reference Electrode)
SM60-T1 (Temperature Electrode Pt1000)
FP20-S13 (Mtg. Kit for Ref. Electrode)
WU20-PCXX (X meters Electrode Cable)
K1500FV (Solution Ground Cable)
K1520VA (250 ml, 3.3M KCl Solution)
K1500GN (O-ring Set for FF20 stainless steel holders)
K1500GP (O-ring Set for FF20 plastic holders)
M1100EU (NIST buffer solution kit 1 pint each of 4.01, 6.86, 9.18)