Diagnostic Information

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 and – 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.

To view the diagnostics on the PH450:

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.

To view the diagnostics on the PH202:

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)].

Asymmetry Potential:

The Asymmetry Potential (AS) also referred to as the millivolt offset, is an indication of the condition of the reference electrode. Theoretically when the electrodes are placed in a buffer 7, the millivolt output from the electrode pair (pH and reference) should be zero. This is seldom the case because there are many small potentials inherent to the electrodes. When a 7 buffer calibration is performed, these potentials are negated and the output is adjusted to zero millivolts. Typically after the first calibration there will be a small offset (either positive or negative) from zero millivolts and as the electrode ages, the offset will become greater. Each time a 7 buffer calibration is performed the asymmetry potential is set to zero and the new adjusted millivolt offset is shown on the second line display (AS). Typically only small changes in the asymmetry potential should be noticed after each calibration. As the millivolt offset becomes greater, the electrode will have a tendency to drift over time and more frequent calibrations will be required to compensate for the drift. Some of the causes of the millivolt offset are depletion of the Potassium Chloride (KCl) from the reference electrolyte. This is common in gel-filled reference electrodes used in high purity water applications. When the concentrated reference electrolyte (KCl) and the low conductivity (mineral free) process solution meet at the reference

junction, the process solution leaches the salt from the reference electrolyte causing the reference potential to become unstable. Another reason is the reference electrolyte becomes poisoned with the process solution. This is most evident in process applications where the process pressure is greater then 1 ATM. When the process pressure is greater then the pressure inside the electrode, the process solution is forced into the reference electrode, contaminating the electrolyte and changing it's potential. When the millivolt offset is ±30 - 45mV, it advisable to replace the reference electrode. The factory defaults for the correction limits in the pH402 are ±120mV. Outside this range an E2 error message will appear in the lower display. The default alarm limits can be adjusted in Service Code 21. Please refer to the Instruction Manual.

Slope:

The Slope (*SL*) also referred to, as the efficiency of the electrode is an indication of the condition of the pH electrode. The slope is displayed in a percentage (%) value, with 100% SL being ideal. When a pH electrode is immersed in a solution, an exchange equilibrium is established between the hydrogen ions in the solution and the ions in the pH glass membrane. This equilibrium is the source of the measured potential. Theoretically for each pH unit change, the millivolt output from the electrode should be ±59.16mV at 25 °C, with pH 7 equal to zero mV. At pH 4 the ideal output would be +177.5 mV at 25 °C (59.16 x 3 = 177.5). This is seldom the case. For example, when the electrode is place in a 4 buffer, the pH value might be 4.12 pH instead of 4.01 and the millivolt output from the electrode might be +173 mV. When a calibration is performed, the pH meter adjusts the 4.12 reading to 4.01 and now +173 mV equals pH 4 instead of +177.5 mV. The instrument then calculates the actual millivolt value vs. the theoretical value (+173 mV ¸ +177.5 mV. = 97.4%) and displays the value as a percentage. When the electrode is new, the slope should be in the upper 90% range. As the electrode ages and loses efficiency, the slope and response of the electrode will start to decrease. The slope value is up dated each time a two-point calibration is performed and usually only small changes in the slope value should be noticed. One of the main reasons the electrode may have a low slope value is because it was not cleaned before calibration, making it less efficient. If a low slope value is noticed, clean the electrode with a 5-10% HCl solution for a minute, rinse it thoroughly with clean water and recalibrate. Depending on the application and response time required, it is advisable to replace the pH electrode when the slope value is in the mid to low 80% range. The factory default values are 70% - 110% of theoretical. When the calculated slope exceeds the programmed values, an E3 error message will appear in the lower display. The default values can be adjusted in Service Code 22. Please refer to the Instruction Manual.

Reference Impedance:

The Reference Impedance (*Z2.*) also referred to as the resistance of the reference junction, is an indication if a precipitate (blockage) has formed in the reference junction. The reference resistance is also influenced by the conductivity of the process solution. In low conductivity solutions (i.e. Ultra-pure water), the conductivity of the solution and the flow rate past the reference electrode effect the RZ value. Typically a clean reference junction will have a resistance of less then 10-15 K Ohms, but in low conductivity solutions, RZ values between 200 and 500 K Ohms are not uncommon. The reference junction provides an electrolytic interface between the reference electrolyte and the process solution. The purpose of the reference junction is to allow a small controlled amount of reference electrolyte to diffuse into the process solution, completing the pH measuring electrode circuit. Most reference electrolytes contain 3 M Potassium Chloride (KCl), saturated with Silver Chloride (AgCl). Process solutions containing

sulfides or sulfur bearing species, react with the silver chloride in the reference electrolyte, causing insoluble precipitates to form in the reference junction. These precipitates cause a high electrical junction resistance, which leads to non-reproducible diffusion potentials, causing the electrode to have a slow constant upward drift. When the RZ value starts to approach 30 -45 K Ohms, the electrode will start to have a slow upward drift. When the reference impedance exceeds the factory default of 100 K Ohms an E5.2 error message will appear in the lower display. The Reference electrode Impedance value can be adjusted in Service Code 04. Please refer to the Instruction Manual.