

Electrode Systems for High Purity Water Applications

1 Introduction

There are many myths associated with the measurement of pH in low conductivity waters and the question of the sample conductivity at which you change from one type of pH electrode system to another is debatable. There is no fixed change over point, in general, all pH systems will work initially, however some pH systems will perform in low conductivity waters for longer periods without manual intervention and are less susceptible to drift due to changes in sample flow rate than others.

This Technical Guide highlights the issues regarding pH measurement in high purity water applications and provides advice of the selection of the different pH systems.

2 Details

The problems, which may be encountered, are:

1. Discrepancies between laboratory grab sample checks and on-line readings.
2. The sample has very few ions in solution (with conductivity values typically between 0.055 and $20\mu\text{Scm}^{-1}$) so the solution resistance is very high can result in drift and instability.
3. Static generated on surfaces of plastic pipework, flowcell, and electrodes, which is dependent on flowrate can result in drift and instability.
4. Reduced flowrate of KCl at the reference junction due to blockages causing an increase in junction resistance can result in drift and instability.
5. The sample has a high temperature coefficient can result in errors in the reading.
6. Temperature of the sample is very different from that of the buffer solution can result in errors in the reading.
7. Confusion that exists regarding the many different buffer solution values available can result in errors in the reading.

3 Suitable pH Systems

ABB would recommend the 7660 pH Electrode System as the ultimate system, which would be suitable for use on ultra pure water samples, as it has a stainless steel flowcell, which is then earthed (grounded), and a flowing reference junction. The stainless steel flowcell will reduce (not eliminate) drift in reading with changes in sample flowrate. The flowing junction will provide a more stable potential at the KCl to sample interface, again reducing the effect on the reading of sample flow changes. It also has the advantage of greatly reducing the possibilities of blockage of the junction maintaining a low reference junction.

Under normal operation the glass electrode and the reference electrode will last for several years as long as the KCl level in the reference reservoir is maintained and the ceramic junction is replaced every 6 to 12 months. With any pH system, the sample flowrate should be as low as possible, 50mlmin⁻¹ would be preferable. This system has a higher initial cost but the long-term cost of ownership to the end user will be significantly lower and it will also provide higher measurement integrity.

Systems such as 7651 and the AP100 can be used on low conductivity samples. However, the penalty will be increased levels of manual intervention for maintenance, the cost of electrode replacement, and greater care will be required in the control of the sample flow rate (50mlmin⁻¹ and constant).

The 7651 system has a plastic flowcell and sealed reference electrode. However, it can be converted to reservoir fed reference type by fitting a reservoir feed to this system, packing the lower part of the reference system with KCl slurry and filling the reservoir with saturated KCl. This will result in a considerable reduction in time spent maintaining the system.

The AP100 has a sealed reference electrode and optional stainless steel flowcell. This will give similar performance but once the KCl slurry is depleted, the AP100 sensor needs to be replaced. In general, the lower the conductivity of the sample the more rapidly the KCl would be depleted.

The 7651 and the AP100 Systems are popular with contractors because of their lower initial cost, but their long-term cost of ownership will be higher. Both electrodes have replaceable reference junctions that would need replacing every 6 to 12 months.

Note. The AP121, AP300, and TB5 pH electrodes are not recommended for high purity water applications, because of their solid-state reference construction, the KCl would be rapidly depleted causing drift in a very short period in use.

4 How to overcome the problems

1. Laboratory grab samples must be taken anaerobically to avoid contamination due to contact with air. Use dedicated containers.
2. Carry out the laboratory determination with the sample at the same temperature as that of the sample passing through the on-line flowcell.
3. If 1) and / or 2) are not possible, bring the laboratory meter to the sample point and measure with the electrode in an overflowing sample container. It would be necessary to switch off sample temperature coefficient during this test.
4. Ensure that the stainless steel flowcell is adequately earthed (grounded). Where a plastic flowcell is used, ensure that stainless steel pipe work is used to and from the pH flowcell and that this pipe work again is adequately earthed (grounded).
5. Control the sample flow rate to a constant level, typically 50mlmin⁻¹.
6. Ensure there is no possibility of air ingress in the sample lines.
7. Prior to calibration, allow the electrodes to stabilise at the buffer solution temperature, e.g. 30mins.
8. Ensure the correct data for chosen buffer solutions are programmed into the transmitter.
9. If calibrating in Manual Mode, enter the correct value at the buffer temperature.
10. Use a 5 fold diluted 9 or 10pH buffer solution for routine single point calibrations, prepared fresh before use (the error can be around 0.1pH).
11. Do not use a 10pH buffer with Low Resistance Glass pH Electrodes (1722 000, AP101-300, AP102-3XX, and AP103-300) due to their sodium error.
12. Use the same buffer solutions for the laboratory meter.
13. Always use fresh solutions, do not repeatedly reuse solutions.
14. Ensure that the correct sample temperature coefficient is programmed into the instrument to enable the readings to be calculated for 25°C.
15. Replace the reference junction on a frequent basis, e.g. 6 to 12 months.
16. Ensure that the reference filling solution is fully saturated.

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