

Discrepancies Between On-line and Laboratory Grab Sample Results

1 Introduction

In comparison to other analytical on-line measurements, pH is considered to be a simple, straightforward parameter with few problems. In many instances this is the case, but there are several critical applications where the nature of the sample and the degree of accuracy expected can make it very difficult to obtain good agreement between on-line and laboratory grab sample results. Such applications include pH measurement in samples where the conductivity values are below 100 μ S/cm, e.g. high purity water in steam raising plant, and potable water treatment using "thin" raw waters. Sample temperature is another factor that is frequently overlooked; ignoring it can introduce errors or increase disagreement between the two methods.

This Technical Guide highlights the possible reasons for these discrepancies, describes their causes, and possible actions to reduce or overcome the problem.

2 Details

Always remember that most problems often occur from more than one cause; each one must be systematically investigated to remove the overall discrepancy.

1. Contamination of the sample by exposure to air.

If low conductivity samples are allowed to come in contact with air, they are very susceptible to carbon dioxide absorption, which will reduce the pH value. In these applications, the on-line pH measurement is always carried out in an enclosed flowcell that excludes air from the sample (unless there is air ingress into the sample line due to leaks). However, the grab sample is often taken to the laboratory in an open container! In these circumstances the pH can be modified long before the measurement is taken.

Ideally, the independent measurement should be made close to the on-line measurement; indeed, this is essential when trying to identify possible causes of disagreement. This is achieved by connecting a flexible tube to the grab sample point and placing the other end into a container. The pH laboratory electrode is then placed in the container where the sample is left to constantly overflow.

If samples are taken back to the laboratory for testing they must be transported in enclosed containers such that contact with air is kept to an absolute minimum, i.e. a full and stoppered glass bottles. Contact with air in the laboratory must also be kept to a minimum whilst the measurement is being taken.

The degree of contamination depends greatly on the conductivity of the sample. Below 100 μ S/cm, the problem is often noticeable, below 10 μ S/cm, the problem is significant, and below 0.5 μ S/cm, the problem will certainly be very severe.

2. Low Resistance (blue glass) pH Glass Electrode.

The use of the Low Resistance pH Glass Electrode in power industry applications and potable water treatment is widespread. This is due to its more rapid response time than General Purpose pH Glass Electrodes (yellow glass) especially at low temperature, i.e. below 20°C, samples, making it an ideal electrode for these applications. However, the pH range is limited to 10pH because at high values the electrode has a small response to sodium. This will cause interference and introduce errors in the reading.

a. pH Calibration.

Some organisations prefer the use of 10pH buffer as one solution for calibration. Unfortunately this buffer is based on sodium compounds. Electrode calibration using this buffer will suppress the electrode slope value at this pH by up to 7%, leading to high pH readings on sample.

To overcome this problem there are two alternatives:

Use a 9.23pH buffer solution for calibration. There is no reason why a 10pH buffer should be preferred, in fact, due to its greater temperature coefficient, if this is not taken into account during calibration, large errors can be introduced, see Point 3.

Use a General Purpose pH Glass Electrode. The performance of the two electrodes, in terms of accuracy, is the same below 10pH. The General Purpose pH Electrode will exhibit a longer response time at low temperatures so it is only critical in few instances.

b. pH measurements above 10pH.

Due to the limitation of the pH range of the Low Resistance pH Glass Electrode above 10pH, the only acceptable solution is to use the General Purpose pH Electrode. Again, the only penalty will be a longer response time at low temperatures.

3. Buffer Solution Temperature Coefficient.

All buffer solutions used for pH calibration have pH values that are affected by temperature, but this variation is dependent on the particular solution. This is known as the Solution Temperature Coefficient. The AX460 and the 4630/35 pH Transmitters have a built-in feature (known as Auto Calibration Mode) with ABB buffer values of 4.00 and 9.23pH (these are the values at 20°C). Calibration in Auto Mode utilises the temperature compensator to measure the temperature of the buffer solution; then the system automatically enters the appropriate pH value. It is always better to buffer close to the same temperature as the sample, but if this is not the case, it is important to allow the pH electrodes to temperature equilibrate in the buffer solution for up to 30 minutes before initiating the calibrating procedure.

For the vast majority of applications, i.e. samples between 2 and 11pH, the 4.00 and 9.23pH buffer solutions are perfectly suitable. Unfortunately other solutions are occasionally used in some organisations because they are an internal standard. This is often due to their source of supply or because they are accommodating other pH meters which are less versatile. If these alternative buffer solutions are used, the following procedure is essential:

- a. Allow the pH electrodes to temperature equilibrate in the buffer solution for up to 30 minutes before initiating the calibrating procedure.
- b. Measure the temperature of the buffer solution at the time of calibration.
- c. Determine the pH value of the buffer solution at this temperature from information supplied with the buffer or from the supplier.
- d. Enter this pH value into the transmitter when prompted.

4. Sample Temperature Coefficient.

Like buffer solutions, the sample is subject to change of pH value as its temperature changes. The temperature coefficient of the 9.23pH buffer is $-0.008\text{pH}/^{\circ}\text{C}$. But where ammonia or sodium hydroxide is used to control the pH in high-pressure boilers, for example, the sample temperature coefficient is $-0.035\text{pH}/^{\circ}\text{C}$. Samples containing other chemical additives could have different coefficients, but this has to be determined for the actual sample on site.

Where sample temperature varies, or where the laboratory grab sample is measured at a different temperature than the sample, differences in the two readings is to be expected. This is overcome if the sample is manually calculated to a standard reference temperature using the predetermined temperature coefficient for that particular sample.

Almost all pH instruments have built-in temperature compensation, but this is intended to compensate for changes in the output of the pH electrode pair, not compensate for the sample coefficient. Unfortunately this is not fully appreciated by the average user. The 4630/35 Transmitter does incorporate the option of applying sample temperature compensation that refers the pH value to a reference temperature of 25°C . However, the appropriate coefficient for the sample must be entered in the parameter setup in the software scrolls. As already stated, ammonia and sodium hydroxide have a coefficient of $-0.035\text{pH}/^{\circ}\text{C}$, but di-sodium and tri-sodium orthophosphate, used in low-pressure boilers, have temperature coefficients of approximately -0.02 and $-0.03\text{pH}/^{\circ}\text{C}$ respectively. It is not always possible to predict the coefficient for a particular sample, so it becomes the responsibility of the user to determine this value.

Note. This feature could be used in various applications but its main application is on high purity water applications such as steam raising plant. To be effective, the chemical composition of the sample must be constant which will result in a constant coefficient.

Two last points to remember:

- a. Always suspect the laboratory method. Points 1, 2, and 3 apply equally to this measurement as well. Point 4 assumes that the laboratory measurement is being carried out at 25°C , if not, this also needs to be taken into consideration.
- b. Always use fresh solutions. It is always a good policy to use the same solutions, prepared from the same batch, for the calibration of laboratory and on-line instruments.

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