

How should I compare grab sample and on-line pH measurements?

Preface: There are potential problems when comparing a laboratory pH analysis or grab sample measurement with on-line pH measurement. In order to obtain reliable data when making comparisons between these two types of pH measurements, it is essential that the proper apparatus and procedures be incorporated as outlined below:

Apparatus: There are many types of pH electrodes and pH meters used in the laboratory and the proper selection of this equipment is important. In order to obtain valid comparative data, the lab grab-sample pH equipment used must be as capable as the on-line pH equipment.

1. Lab pH Meter — A top quality pH meter, portable or benchtop design, with automatic temperature compensation and an input impedance greater than 10¹² is required. The direct readout of the pH electrode output signal in mV is a desired feature for this pH meter.
2. Lab pH Electrode — Many lab pH electrodes are not suitable for making comparative measurements due to their physical design, their electrochemical design (e.g. type of glass membrane, type and viscosity of reference electrolyte, number of salt bridges), type of element (e.g. Ag/AgCl or Hg/Hg₂Cl₂), and the type, size, and material of construction used for the reference liquid junction.

A lab or grab sample pH electrode should be selected which closely matches all of the design characteristics of the pH electrode used in the on-line pH sensor. Often times the same design of electrode or sensor used in the process is also used for the lab grab sample. Many lab pH electrodes will not tolerate the on-line process conditions or the rugged handling required to obtain a 'representative' grab sample. The difference in the performance of two dissimilar electrode designs will contribute to a difference in the pH readings obtained. When combined with the concerns listed below, this can add up to a significant comparison 'error'.

Considerations: Following a simple, but rigorous procedure every time will improve the repeatability in the data obtained from comparative grab sample and on-line pH measurements. Disagreements between these two comparative pH measurements are often caused by:

1. Temperature — In addition to the automatic temperature compensation, care should be taken to ensure that the temperature of the grab sample is kept at the exact temperature as the on-line process temperature. Each process media may have a significant pH temperature coefficient depending upon its chemical constituency. The pH value of a given solution may change due to a change in the grab sample temperature (i.e. the automatic temperature compensator device does not correct for this). Avoid time delays between grabbing the sample and measuring its pH value.
2. Volatile Constituents — Grab samples, when exposed to the atmosphere, will permit the off-gassing of any volatile constituents which could alter the pH of the grab sample. When this is a concern, grab samples should be collected in a properly designed and sealed chamber which contains the sample's pH and T.C. electrodes. Time delays between grabbing the sample and measuring its pH value should be avoided.

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3. Atmospheric Contamination — Permitting the grab samples with a pH greater than 7.0 to be exposed to the CO₂ in the atmosphere could result in the additional formation of carbonic acid in the sample, resulting in a lowering of the sample's pH value. This situation most often occurs when the grab sample is first taken in an open container or when the lab pH electrodes are introduced to the sample after opening a sealed container. Standard laboratory practices often call for the sample to be stirred before and/or during the measurement of its pH value. If stirring occurs in an open container, volatile constituents will off-gas and CO₂ will be absorbed.

pH Calibration Technique: When a grab sample pH measurement is used to calibrate or validate the on-line pH measurement, the technique used should not introduce an error. The most common cause found for discrepancies between grab sample and on-line pH measurements is a faulty technique. The following pH calibration technique is recommended:

1. The laboratory pH measurement equipment should be routinely verified by performing a two-point pH buffer calibration.
2. The on-line pH measurement equipment should receive a two-point pH buffer calibration when first put into service or when the pH electrodes are replaced.
3. Record the on-line pH meter reading at the same instant the grab sample is taken.
4. The grab sample pH should be measured without time delays.
5. Record the pH value of the grab sample and compare it to the on-line reading in step # 3 above.
6. Adjust the on-line pH meter for the change in pH measurements between the readings in steps #3 & #5. A common mistake is to adjust the on-line meter to read the same pH value as the lab meter. This would introduce a significant 'error' especially if there had been a time delay between the comparison pH readings during which the on-line pH value had actually changed.
7. Establish a limit for the allowable change in pH between the comparison pH measurements before the on-line pH instrument is to be adjusted (e.g. maximum allowable change in pH is < 0.1 pH unit). Attempting to adjust for smaller pH values (e.g. ± 0.005 pH units) often introduces an error for the sake of 'fine tuning' the pH reading.

When small changes in pH readings occur and one is in doubt as to which pH reading is correct, we favor accepting the on-line pH reading since its measurement electrode is acclimated to the process conditions while the lab pH electrode is usually not.

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