

Introduction to pH Instrumentation

Single or Multiparameter Instrumentation

Depending on the requirements of the application, users may need to measure only one parameter such as pH or a group of parameters such as pH, ORP, EC, TDS, temperature and others. From benchtops to complete systems and from portables to testers, HANNA provides solutions in all categories of instrumentation.

The HANNA single parameter instrument offers the advantage of simplicity and focus in the requested parameter needs. The advantage of HANNA multiparameter instruments is that a user can choose a single meter packed with all the requirements they need to meet the demands of their application.

Multiparameter instruments offer different operating solutions that tailor to a user's real-world needs: multiparameter meters that can measure two or three parameters, but only one per time or multiparameter meters that offer two or three parameters measured simultaneously—useful on experimental and research applications where the influence between the parameters is important to be known. Multiple inputs provide the capability for simultaneous measurement.

pH Measurement Input

Different input solutions are available for HANNA instrumentation according with the type of the electrode selected by the user: a BNC connection for combined pH electrodes or a half cell electrode and reference probe using a separated reference input. A DIN connector is used to connect amplified and intelligent pH electrodes. Electrodes utilizing a DIN connection are usually combined and feature a built-in temperature sensor.

Temperature Input

Temperature is measured to compensate for temperature in pH readings. For HANNA meters featuring temperature compensation, a separate temperature probe is usually supplied with the instrument or the pH probe features a temperature sensor built-in. If a temperature input is not present, many instruments still offer the ability to manually adjust the temperature according with an external temperature reference.

pH Temperature Compensation

pH readings must be temperature compensated. The source of temperature measurement could be from a temperature sensor or from a trimmer that is manually adjusted. In any case, the instrument is correcting the pH reading with temperature.

mV Reading

HANNA meters with this feature can offer the ability to read two different parameters expressed in mV; the pH when the input probe is a pH electrode or ORP if an ORP probe is connected. The mV relative mode permits a calibration of the input expressed in mV.

pH Calibration

pH calibration should be performed daily or every time when a new lot of readings is started. Any kind of errors during the calibration will affect all the readings until a new calibration is performed. Errors during the calibration process can be eliminated if standard calibration procedures are followed.

Some of the requirements of the standard calibration procedure::

- 1) To clean and activate the pH electrode before the calibration
- 2) To use only fresh pH buffers
- 3) To respect the measurement and rinsing steps during calibration to avoid any kind of buffer contamination.
- 4) To wait for full stability before a new calibration point is confirmed
- 5) To have a correct temperature compensation of pH reading and pH buffers.

Based on the conclusion that one of the most important step that have to be done to have good readings during the standard pH measurement is calibration. HANNA pH instruments are supplied with a starter package of solutions to assure this.

pH Calibration Check™

Many instruments feature HANNA's exclusive pH Calibration Check™ technology. Calibration Check™ is a diagnostics system that ensures accurate pH readings every time. By alerting users of potential problems during the calibration process, the Calibration Check™ system eliminates erroneous readings due to dirty or faulty pH electrodes or contaminated pH buffer solutions during calibration.

Throughout the calibration process, users are guided step-by-step by the on-screen tutorial. After calibration, the probe condition and response time is evaluated and an electrode condition and response time graph is displayed informing the user of the overall pH electrode status.

Calibration Errors

Instruments utilizing HANNA's Calibration Check™ technology can evaluate an electrode during calibration and store a history of parameters that describe the quality of electrode to be compared from one calibration to another. During calibration, a very small degradation of these parameters is normal and can be expected. A big change in the parameters signifies an error in the calibration procedure such as a dirty electrode before the calibration.

pH Buffer Contamination

pH buffers can be contaminated during the calibration procedure by numerous factors such as introducing a contaminated probe, using old buffers, or by reusing buffers. With these factors, the calibration of the instrument and subsequent measurements will be wrong.

Contaminated buffer issues can be detected during calibration by HANNA instrumentation with Calibration Check™. Warning messages can be generated to inform users about the identified issue.

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Response Time of Electrodes

Another parameter that is evaluated during the calibration with Calibration Check™ technology is the response time of an electrode. This is evaluated based on the measurement of time necessary to reach stability when the electrode is immersed in a new buffer that has a difference in pH larger than 3 pH units from the old one.

Offset and Slope of pH Electrode

The offset and slope are the most important parameters that can describe the quality of an electrode. It is important for a measurement process determination to be stable and accurate.

With HANNA's calibration Check™ technology, the offset of the electrode can be evaluated after one point calibration. Common sense is asking to be 7.00 pH buffer, but HANNA instruments using Calibration Check™ are able to determine the offset based on any calibration point. The accepted range for offset is ± 30 mV. A minimum 2 calibration points is necessary to determine the slope. Between any two calibration points the slope can be evaluated and normally has to be in a range of 80% to 110 %, where the 100% is 59.16 mV/pH @ 25°C.

Calibration Points and pH buffers

The calibration of pH electrodes is performed normally in 2 points: 7 pH, and 4 or 10 pH. This is based on the assumption that the pH electrode is linear from 3 pH up to 10 pH. For the most accurate reading, it is a good practice to calibrate to a point closest to the values received during normal measurement. For a variety of applications and measuring points, many HANNA meters offer the ability to calibrate in more than 2 points, such as 3 points up to 5 points being common. Many instruments can recognize up to 7 calibration pH buffers: 1.68, 3.00, 4.01, 6.86, 7.01, 9.18, 10.01 and 12.45 to cover the entire pH range. The recognized pH buffers are temperature compensated by the instrument which is necessary due to pH variation of buffers due to temperature. For example, a 7.01 pH buffer is 7.01 pH only @ 25°C. A table of temperature variation is printed on the label of each pH buffer .

Custom pH Buffers

HANNA has implemented the concept of custom pH buffers into many of its instruments. This concept solves two different issues: to use non-standard pH buffers or to permit in-line calibration using a reference pH meter that measures the pH of similar sample. In both cases, temperature compensation cannot be performed because the temperature variation correlation is unknown.

Stability During the Calibration

A readings stability has to be reached in order to avoid a wrong calibration. Based on this, the confirmation of a new calibration point is done only after stability criteria is reached. Users are informed during all processes about the stability conditions before the user confirms a stable condition, and any instability will restart the stability evaluation. The stability criteria during the calibration

is more rigorous than during the measurement. This mode used in HANNA instrumentation avoids errors by confirmation of calibration points during unstable readings. This principle is respected in any type of calibration: manual or automatic confirmation.

Out of Calibration Range

This is an important feature during measurement and is part of GLP (Good Laboratory Practice). Based on the calibration points where the instrument was calibrated, the measurement is considered accurate or not. If the measurement reading is in a range far from the calibration points, the "Out of calibration range" message is displayed. The measured value is shown and the user can use it, but with the warning from instrument related to possible inaccuracy.

Calibration Time-out

The Calibration Time Out, like Out of Calibration Range are warning messages from GLP (good laboratory practice). Proper, scheduled calibrations are crucial for accurate and repeatable measurements. In the event that readings are performed after an unacceptable time has passed since last calibration, a warning reminder will be displayed. The reading can still be performed and used, but under the condition imposed by the warnings.

Step by Step Calibration

In order to avoid errors during the calibration procedure, the meters display indicators that can be followed by the user for a successful calibration. If necessary, it is possible for the calibration steps to be performed in a different order by the user.

Additional Features

GLP (Good Laboratory Practice) and ISO standards are used to request the traceability of operations. HANNA's GLP solutions offer support for quality of calibration plus all the necessary information to identify the instrument, operator and the moment when the calibration was done.

Logging is a common feature for many instruments and can be used to memorize readings. Two working modes are available: log-on-demand and automatic or interval logging. With Log-on-demand, measurements that are considered important by the user will be saved by request upon pressing the log button. With automatic or interval logging, the instrument saves all the readings according with a specified interval. Another logging mode is AutoEnd logging or log on stability.

Analog output is a feature used to connect the instrument to a recorder to record the measurement in analog mode. The common ranges of analog output are 4 - 20 mA or 0 - 20 mA and 0 to 5V.

The graphic LCD that many HANNA meters include improve the user experience with features such as tutorials, contextual help, multi-language support and icons and messages to guide the user through operation and calibration.