



Electro-Analytical Measurement Algorithms

Measurements in General

All measurements are prone to **Measurement Errors**. A measurement is not complete without the evaluation of the error-range / tolerance-range.

Accuracy is the degree of agreement between the measured and the true value.

Precision is the degree of agreement between replicate measurements.

Frequent **Calibrations / Re-calibrations** reduce errors. The frequency of re-calibrations depends on the drift of the sensor signal and the drift of the transducer/signal converter.

The drift of modern transducers is generally neglectable. pH electrodes however are based on electrochemical reactions, which are not very stable.

pH electrodes need calibration when the measuring conditions change (new sample with very different composition) and re-calibration when the measurement takes more time (usual re-calibration after one day).

Sensor signals, especially low-level signals can carry a high percentage of **Noise**. This noise usually has a periodic and a random component.

pH measurements are prone to picking up noise, especially measurements with microelectrodes and the reference input not bound to ground.

The reason is the very high resistance of the electrode membrane, which enforces the use of electrometer amplifiers, which capture the slightest signal, which is picked up by the electrode cable

Noise is usually not seen when measuring with meters because the slow Analog/Digital converters within the meter integrate over a certain time and filter out the noise. Data acquisition systems show the noise component more clearly. **Signal Averaging** and regression methods usually eliminate negative effects.

Temperature Measurements

Temperature changes are usually slow (not always, e.g. explosion) and most temperature sensors react also rather slowly (reaction time), but it is always necessary to compare the dynamics of the process with the dynamics of the sensor.

In case of static or pseudo-static (very slow changes) measurements the reading should be taken a certain time (waiting time, stabilisation time) after the probe is immersed in the sample.

The time constant (reaction time) of a temperature sensor is not a fixed value; it varies with the sample medium, the movement of the medium, the temperature difference and the immersion length of the sensor

Other important points which have to be considered is the influence of the sensor on the sample in case of small sample quantities and the necessary immersion length for a good accuracy of the measurement.

For very precise measurements a calibration is recommended. It is a comparison measurement where the temperature of the medium is known within close tolerance limits. Usually not only the sensor but the whole measurement system is calibrated.

pH Measurements

pH is a measure of the acidity or alkalinity of a solution.

pH is defined as the negative Logarithm of the Hydrogen ion concentration.

For example pH =2 means the Hydrogen ion concentration is 10^{-2} mol/L.

Related to the concentration the pH scale is extremely non-linear:

A solution with pH = 2 has a 1000 times higher Hydrogen ion concentration than a solution with pH = 5.

pH values generally range from 0 to 14, with a pH value of 7 being the neutral point (the value of pure water). The values above the neutral point (7 to 14) represent increasing alkalinity, whereas pH values below the neutral point (7 to 0) represent increasing acidity.

- Strong Acid pH = 0
- Lemon Juice pH = 2
- Milk pH = 6.6
- Pure Water pH = 7
- Baking Soda pH = 8
- Ammonia pH = 12
- Strong Base pH = 14

The sensor to measure pH is usually a pH combination electrode (housing the pH system and the needed reference system within one electrode body).

This electrochemical sensor delivers a mV (millivolt) signal, which is in a wide range (linear range approximately from pH 2 to pH 10) proportional to the pH value.

The theoretical slope S at 25 °C is 59.16 mV pro pH unit

The slope increases with the temperature t (°C), the relation is:

$$S_t = S_{25} \times \frac{273.16 + t}{273.16 + 25}$$

The theoretical voltage at pH 7 is 0.00 mV

Positive mV values indicate acidity, negative mV values indicate alkalinity.

In reality the slope is between 50 and 58 and the offset voltage at pH 7 is in the range of ± 30 mV. Good pH electrodes have values closer to the theoretical values.

Shielding and grounding is an important issue for pH measurements.

The usual configuration of pH electrodes uses the core of the coaxial cable to transmit the electrode signal and the shield of the coaxial cable to transmit the reference signal.

This works well in most applications because the reference input is usually connected to ground and therefore the shield is grounded and can fulfill its shielding function.

In some applications it could be necessary not to connect the reference input to the ground to avoid ground loops. Then both sides of the pH electrode inputs (core and shield of the BNC cable) are very high-ohmic and have no connection to ground. This configuration needs enhanced noise filtering because the shield of the BNC cable acts like an antenna and picks up noise.

Calibration

Since the electrochemical potential of an electro-analytical measurement is not precisely defined it is necessary to do a calibration.

In case of a pH calibration the electrochemical potential (mV) of the pH electrode is measured and stored while the electrode is immersed in buffer solutions with exact defined pH values. Point to point linear interpolation between the various measuring points represents the calibration curve of the pH measuring system.

Calibration of a pH measurement means always the calibration of the whole measuring system: electrode + amplifier + display/data acquisition system.

A complete calibration procedure contains always an electrode check:

- Level of filling solutions and air bubbles (shake them up)
- Condition of liquid junction (only optical)
- Signal in buffer 7: should be only \pm few mV
- Signal in Buffers 4 and 10: calculate the slopes between 7 to 4 and 7 to 10, are the slopes identical (good linearity)? Are the slopes close to the theoretical value (55 to 59 mV/pH unit)?
- How fast does the electrode react: signal change from one buffer to the other and time till reading is stable?
- Is the reading stable? Signal Drift? Small random signal changes (liquid junction problems)?
- Has the electrode a hysteresis (same reading when coming from a higher level and from a lower level to the same buffer)?
- Compare the values of the latest calibration with previous calibrations. Can you trust the electrode?
- It is necessary to store all data in an arrangement which gives a good overview and allows comparisons between the various calibrations at different times of one electrode and also comparisons of the calibration values of different electrodes.

Re-calibration Procedures

When multiple calibrations have proofed the electrode is trustworthy and the slope is stable, a one-point re-calibration can be sufficient, just to compensate small level shifts of the electrode signal. Use the buffer, which is closest to the actual measurement.

A condition for the simplified re-calibration is, that the general measuring conditions (e.g. sample composition, temperature) have not changed considerably.

When the sample is measured the electrode signal is compared with the calibration curve (linear Interpolation between the next two calibration points).

It is important that the conditions for the calibration and sample measurement are as close together as possible! (Temperature, Ionic Strength, Stirring Speed).

A pH measurement is an ion-selective measurement and the liquid junction potential has a considerable influence on the quality of the measurement. The best results are achieved when the ionic strength of the calibration solution (buffer) and the ionic strength of the sample are identical.

Identical conditions cannot be replaced by calculations; there are multiple influences, which can be only partially calculated.

Do not extrapolate! The sample pH should be within the calibration range.

If during online measurements considerable temperature changes are expected, calibrate with various temperatures to get a group of calibration curves with the temperature as additional parameter. To find the correct sample pH a 3-dimensional interpolation has to be performed: mV-Signal, Temperature, pH.

Millivolt to pH Conversion

pH electrodes deliver a millivolt signal. Since the electrochemical potential of an electro-analytical measurement is not precisely defined it is necessary to calculate the pH value from comparing the electrode millivolt signal of the sample measurement with the calibration curve (see paragraph Calibration).

This millivolt to pH conversion is done by a linear interpolation from the nearest calibration point to the next calibration point in the direction of the sample measurement.

An example will show the whole procedure.

Calibration points:	pH 4.00	+186.0 mV	25.2 °C
	pH 7.00	+12.0 mV	25.2 °C
	pH 10.00	-160.5.0 mV	25.2 °C
Sample measurement:	pH = ?	+55.4 mV	28.6 °C
Nearest calibration point:	pH 7.00	+12.0 mV	
Next calibration Point:	pH 4.00	+186.0 mV	

Gradient of pH over mV = $(4-7) / (186-12) = (-0.01724)$

Millivolt Difference sample to nearest point = $55.4-12 = 43.4$

pH of the sample = $7.00 + 43.4 \times (-0.01724) = 7.00 - 0.75 = 6.25$

This value can be temperature compensated with the formula in the next paragraph.

Temperature Compensation of pH Measurements

The 3 main sources of temperature dependency of pH electrodes are:

1. The membrane function, which follows the Nernst equation.
2. The liquid junction potential, which is commanded by the ion mobility.
3. The membrane resistance.

Only the first component is calculable and can be compensated. The second component can have a considerable influence but cannot be calculated generally because it is depending on the composition of the sample and the filling solution of the electrode. The third component can be neglected when the electrode amplifier has a very low input/bias current, which is the case in this application.

The best way to avoid temperature-related errors is to calibrate at sample temperature. To get a rough idea of the temperature influence:

1°C temperature difference causes a total error of approximately 0.5 %.

In cases of continuous online measurements with changing temperatures, there are two ways of temperature compensation:

- a) Perfect temperature compensation by multiple calibrations at various temperatures and using interpolation between the various calibration curves during the sample measurements.
- b) Partial temperature compensation by calculating the temperature dependence of the Nernst equation:

$$\text{pH}_{\text{comp}} = [(\text{pH}_{\text{meas}} - 7) \times (273.16 + T_{\text{cal}}) / (273.16 + T_{\text{meas}})] + 7$$

This formula is based on the assumption that at pH 7 the electrode signal is zero.

It can be applied for good electrodes where the offset at pH 7 is only few millivolts.

Ion-Selective Measurements

Ion-Selective Measurements can be treated in the same way as pH measurements, by simply replacing the term pH by the term pX, where X is the symbol of the ion, For example pNa would be the Logarithm of the Sodium Concentration.

However a Temperature compensation for Ion-selective measurements is difficult because the point where the electrode signal is zero is usually not known and is mostly in the non-linear range of the calibration curve.

What makes Ion-selective measurements different from pH measurements is the use of another definition of the Ion concentration:

In Ion-selective measurements usually Calibration Standards are used where the Ion concentration is given in ppm (parts per million = mg/L)

For example a calibration is performed with:

1 ppm Ca	defined as $\log C = 0$
10 ppm Ca	defined as $\log C = 1$
100 ppm Ca	defined as $\log C = 2$

C means in this case Concentration of the Calcium ion.

The relation between Concentration (ppm) and the Electrode signal (mV) is logarithmic. The relation between $\log C$ and the Electrode signal (mV) is linear or close to linear.

For example:

The calibration procedure has given:

Electrode Signal E1 = 114.3 mV for a concentration C1 = 1 ppm	$\log C1 = 0$
Electrode Signal E2 = 170.5 mV for a concentration C2 = 10 ppm	$\log C2 = 1$
Electrode Signal E3 = 228.9 mV for a concentration C3 = 100 ppm	$\log C3 = 2$

The sample measurement has given an electrode signal $E_x = 142.3$ mV

We have to find the closest calibration points, which are E1, C1 and E2, C2.

To calculate the sample concentration we have to perform a **logarithmic Interpolation for C**, which means a **linear Interpolation for $\log C$** between E1, $\log C1$ and E2, $\log C2$.

$$\log C_x = \log C1 + (E_x - E1) \times \frac{(\log C2 - \log C1)}{(E2 - E1)} = 0 + 28 \times 1 / 56.2 = 0.498$$

$$\log C_x = 0.498$$

$$C_x = 10 \exp 0.498 = 3.14 \text{ ppm}$$