A CONSIDERATION OF pH MEASUREMENT AND THE ELEMENTS OF THE ANALYSIS SYSTEM

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pH measurements are regularly made in the process industry. This article serves to overview the principle of measurement and to describe the elements of the measuring system.

In this article, we first discuss the measurement system and its constituents. Thereafter, we briefly consider some sources of error inherent in these systems, and some practical issues.

Description of the measurement system

The pH measurement originates in the electrode system, This system consists of a pH sensor or pH Half Cell, whose voltage varies proportionately to the hydrogen ion activity of the solution, and a reference electrode, or Reference Half Cell, which provides a stable and constant reference voltage. The pH electrode consists of a thin membrane of hydrogen sensitive glass blown on the end of an inert glass tube, This tube is filled with an electrolyte, and the signal is carried through Silver/Silverchloride (Ag/AgCl) wire. This is a pH Half Cell.

A similar system, but without using a Hydrogen sensitive glass, is used as a reference. A small filter (diaphragm) connects this tube to the external liquid. This system is called a Reference Half Cell. The meter measures the difference between the pH Half Cell and the Reference Half Cell in millivolts dc. This millivolt reading is read by the unit and displayed in either mV or pH units.

Features of pH electrodes

Electrodes are housed in either plastic or in an all-glass body configuration. They can be either single cells or, as shown in Figure 1, combined into one body for ease of use. Regardless of the configuration, there are several features common to all electrodes, as shown in Figure 1:

- sensing membrane glass: performs actual measurement
- reference junction: acts as a liquid path electrical conductor
- internal reference: supplies a constant equilibrium voltage
- pH internal element: supplies a voltage based on the pH value of the sample
- reference fill hole: used to replace the reference electrolyte solution (not in gel or solid-filled references)

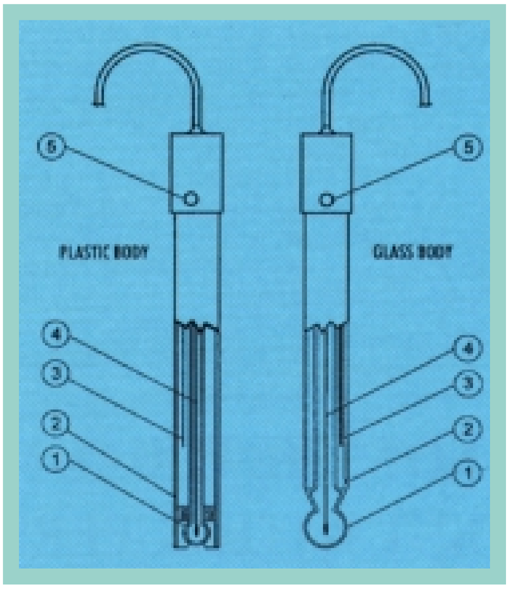

Figure 1
Typical pH electrodes showing their constituents.

pH half cell

Within the cell, the electromotive force is based upon the following equation:

$E_{obs} = E_c + N_f \log a_H$ where:

E_{obs} = observed potential

E_c = reference potential including other stable and fixed potentials

N_f = Nernstian slope factor

a_H = hydrogen ion activity

The slope factor N is called the Nernstian factor and is a characteristic of the glass membrane equal to:

$N_f = 2.3\ RT/nF$ where:

R = gas constant (8.314 J/kMol)

T = absolute temperature in K

F = Faraday constant (9.648×10^4)

n = valence factor (1 in the case of hydrogen)

With R, F and n being constants, the observed potential is therefore dependent on the temperature of the sample. The relationship between the Nernstian factor and temperature is shown in Table 1.

°C	0	10	20	25	30	40	60	80
Nf	54.20	56.18	58.16	59.16	60.15	62.13	66.10	70.07

Table 1
Nernstian factor and temperature relationship

The reference half cell

The silver/silverchloride electrode is formed by electrolyte deposition of silver chloride on a silver wire. The electrode wire is immersed in a potassium chloride solution. Since concentrated chloride solutions dissolve silver chloride through the formation of chloro silver complexes, the potassium chloride solutions are presaturated with silver chloride. Contact with the external solutions is made through a liquid junction.

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Measurement considerations

In this section, we highlight some or the practical issues that can affect this measurement that you make.

The effect of the glass electrodes

The resistance of glass electrodes partially depends on the temperature. The lower

the temperature, the higher the resistance. It requires more time for the reading to stabilise if the resistance is higher. In addition, the response time will suffer to a greater degree at temperatures below 10°C. Since the resistance of the pH electrode is in the range of 200 MW, the current across the membrane is in the pH range. Large currents can disturb the calibration of the electrode for many hours. For these reasons high humidity environments, short circuits and static discharges are detrimental for a stable pH reading. The pH electrode's life also depends on the temperature, as shown in Table 2. If constantly used at high temperatures the electrode life is drastically reduced. The higher the range of temperature, the shorter the life of the electrode.

Ambient temperature	1 - 3 years
90°	less than 4 months
120°	less than 1 month

Table 2
Typical electrode life

Alkaline error

High concentrations of sodium ions interfere in the alkaline solution's reading: the pH at which interference starts to be significant depends upon the composition of the glass. This interference is the alkaline error and causes the pH to be underestimated. Typical errors are shown in Table 3.

Concentration	pH	Error
0.1 Mol/L(Na+)	13.00	0.10
	13.50	0.14
	14.00	0.20
1.0 Mol/L(Na+)	12.50	0.10
	13.00	0.18
	13.50	0.29
	14.00	0.40

Table 3
Sodium ion correction for the Hanna glass formulation

Conclusion

Acidic or alkaline solutions can be easily quantified by pH measurement. However this article has highlighted some of the practical issues that can affect the measurement.

Resume

Pierre Joubert is the National Sales Manager of Hanna Instruments (Pty} Ltd. He has had extensive experience in analytical instrumentation in the laboratory and process fields. His qualifications include a certificate in marketing and an N6 in electronics. He is also a qualified electronic mechanician.