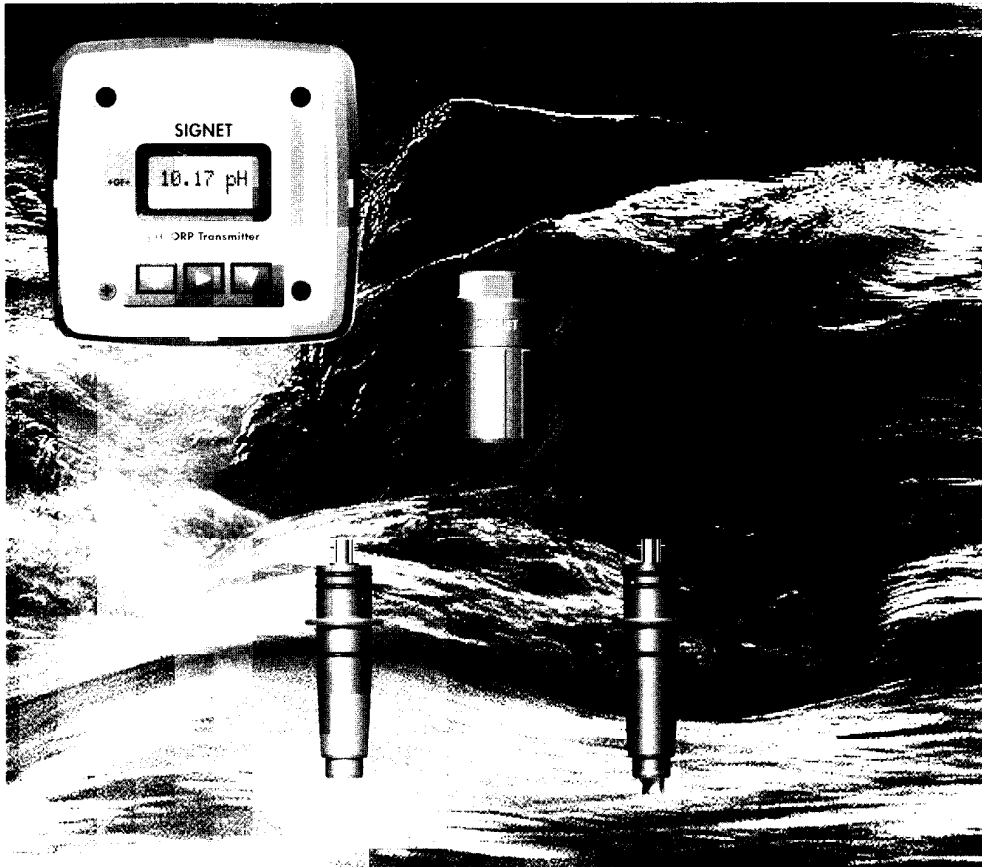


# SIGNET pH, ORP, Conductivity



## Training Manual



**GEORGE FISCHER +GF+**

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# pH, ORP, Conductivity

## Introduction

There are many different characteristics of liquids that are important to their use. In waste treatment, many of these characteristics must be controlled to prevent the waste from upsetting the municipal waste treatment facility, or ultimately, the life in a lake or stream where the waste is discharged. In water treatment, these characteristics can affect the taste, corrosiveness, and drinking safety of the water. For industrial process control, these same characteristics can dramatically affect the performance of a solution for cleaning, etching, plating, or whatever it's primary purpose.

There are hundreds of tests or measurements that can be run on solutions - many very specific such as the concentration of a single specific species in the solution. These tests can also vary depending on whether the species is present in very large amounts (generally measured in % by weight or volume, or ounces per gallon), or in very small amounts (can be measured in parts-per-million (PPM) (also known as mg/l), or even parts-per-billion (PPB). Depending on the species and the concentration, test equipment for these tests can be quite varied, and quite sophisticated.

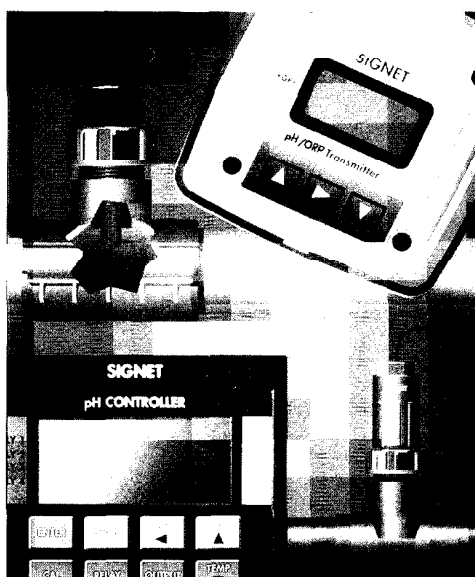
In other analysis, there are measurements for characteristics of solutions that are quite general, but indicate the overall condition of the solution - a sum total of all the contents of the solution that can attribute to the property or characteristic. These measurements have been found to be very important for all water based solutions - because they affect the entire water life cycle on the planet. Three of these measurements include pH, ORP and conductivity.

## pH

pH is a measurement of the acidity or basicity of the solution. Neutral water, H<sub>2</sub>O is made up of an equal number or

H<sup>+</sup> ions and OH<sup>-</sup> ions. If an acid is added to the solution, the balance is shifted, and an excess of H<sup>+</sup> ions is present. Solutions that are acidic can be corrosive, have a sour taste, and react with bases to form water and a salt. When bases are present, an excess of OH<sup>-</sup> ions exists. Solutions that are basic are slippery feeling, bitter tasting, and react with acids to form water and a salt.

The affect on the life cycle of the planet is much more significant. We have all heard of acid rain, and it's affect on both plant and water life. This acid is generated in the atmosphere through a chemical reaction with gases emitted from many sources here on earth. Similarly, if the pH of water discharged into these same lakes and streams in not carefully controlled for pH, the same affect will occur. The delicate process of human waste digestion in a municipal waste treatment plant can also be damaged by the pH of incoming waste. For these reasons, all waste that is discharged to either a municipal treatment facility, or a lake, stream, or ocean, must be carefully monitored and controlled for pH. To help enforce these requirements and



SIGNET sensors & instruments

ensure safe discharge into our municipal plants and water systems, the EPA has set stringent guidelines that must be complied with or else significant fines are levied.

The EPA's primary area of enforcement is with the municipal plants discharging into water systems. These municipal plants in turn regulate the various industries that discharge into their plant, and also will levy large fines for non-compliance with their limits.

## ORP

ORP is a measurement of a solution's ability to oxidize or reduce. Presence of oxidizers in a water system will cause the organics in the system to be oxidized, or destroyed (often called disinfected). Although this is a necessary process for our drinking water, excess oxidizer discharged into a lake or stream will literally kill the ecostructure of that system. Likewise, oxidizers discharged into a municipal waste treatment "digesting" plant, will kill the bugs used to digest the human wastes.

ORP is an important measurement for plants that require oxidation of their waste prior to discharge. Such applications include cyanide oxidation in the plating industry, or waste disinfection in the slaughterhouse industry. Oxidizers can be eliminated by a reaction with a reducing agent. This process is also controlled by ORP. Common oxidizers include chlorine, sodium hypochlorite, ozone, and bromine. Common reducers include sulfur dioxide, sodium sulfite, and ferrous sulfate.

## Conductivity

Conductivity is a measurement of the salts in a solution. The salts present in a solution cause the solution to be conductive, i.e. to conduct electricity. The true value of this measurement is generally not how much electricity the solution can conduct, but instead, it's correlation to the concentration of salts in the solution.

As stated earlier, the neutralization of acids and bases create water and a salt. As a result, two solutions may in fact have neutral pH, but one could be clean enough to drink, while the other is as salty as the ocean. Conductivity enables us to quantify the amount of salts present.

Certainly we are all aware that the ecostructure of the ocean is much different than the ecostructure of a lake or stream. Fish that live in sea water will quickly die if placed in freshwater, and vice-versa. For these reasons, it is important to monitor the conductivity of the water we discharge into these systems. A significant trend in the waste treatment discharge permits of industrial plants is that they must monitor not only their pH, but also their conductivity. Simple neutralization of a waste acid using pH may no longer be acceptable, if the amount of salt produced in the waste causes the conductivity (salt content) to become excessive.

For the treatment of water for drinking, conductivity is able to monitor salt water desalination, and accurately ensure that all of the salt is removed from the water. Many other water treatment processes also depend on conductivity as their primary measurement for the quality of the water produced.

# 1. pH measurements

## 1.1 The pH scale

pH is the term used to define the acidic activity of a solution. For convenience it is a logarithmic scale and compresses the values in the range of about 0–14.

In effect the two ends of the scale correspond to the acidic activities of a strong acid e.g. sulfuric acid with a pH value in the 0 range and at the other end a strong base e.g. caustic soda with a pH around 14.

The formal definition of pH is:

$$\text{pH} = -\log(a_{\text{H}^+})$$

i.e. it is actually the negative logarithm of the hydrogen ion activity. Hydrogen ion (proton) activity is what we have termed before as the acidic activity and in a first approximation is simply the acid concentration.

The highest concentration of the acid used in our example would be fuming hydrochloric acid at 370 g/l (37%) or about 10 mole/l. In this case the pH is  $-\log(10) = -1.0$ .

We see that the pH can take on negative values but cannot go much less than zero. (At high concentrations there is another factor that we have neglected here called activity coefficient. This limits the pH value at the extreme ends of the scale.)

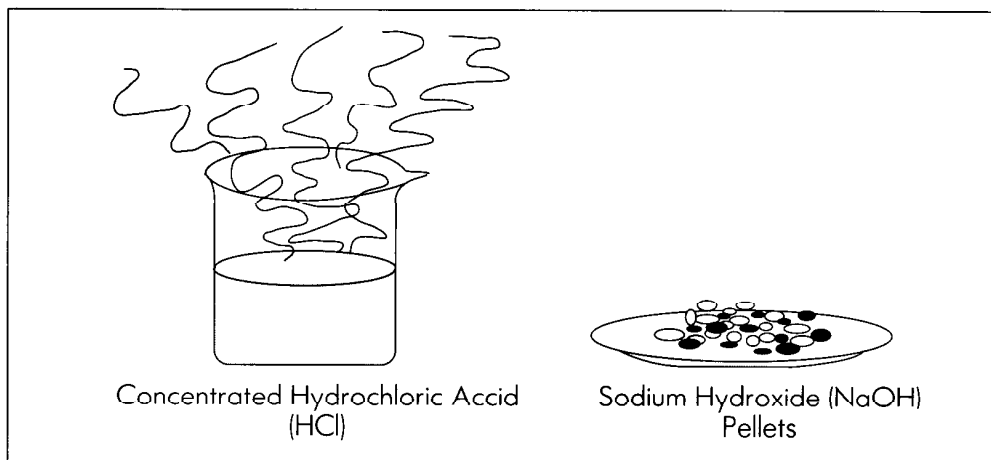
### pH of bases

The other end of the pH scale corresponds to alkaline or basic substances or solutions. If we take an extreme example say pure caustic soda (sodium hydroxide: NaOH) it has no acidity since there are no protons. Its pH would be:

$$\text{pH} = -\log(0) = \text{infinity}$$

Here we see a problem in trying to calculate the pH of a pure and dry alkaline substance.

The pH that we have attempted to calculate lies outside of the scale we expect.



Concentrated acid and base

### pH of acids

Let us take diluted hydrochloric acid (HCl) at a concentration of 36,5 g/l. In the expression for pH it is required that the concentration unit is mole/l. That is the concentration in g/l divided by the molecular weight of the substance. In our case, the hydrochloric acid has a molecular weight of 36,5 g/mole. Thus the concentration is 1 mole/l.

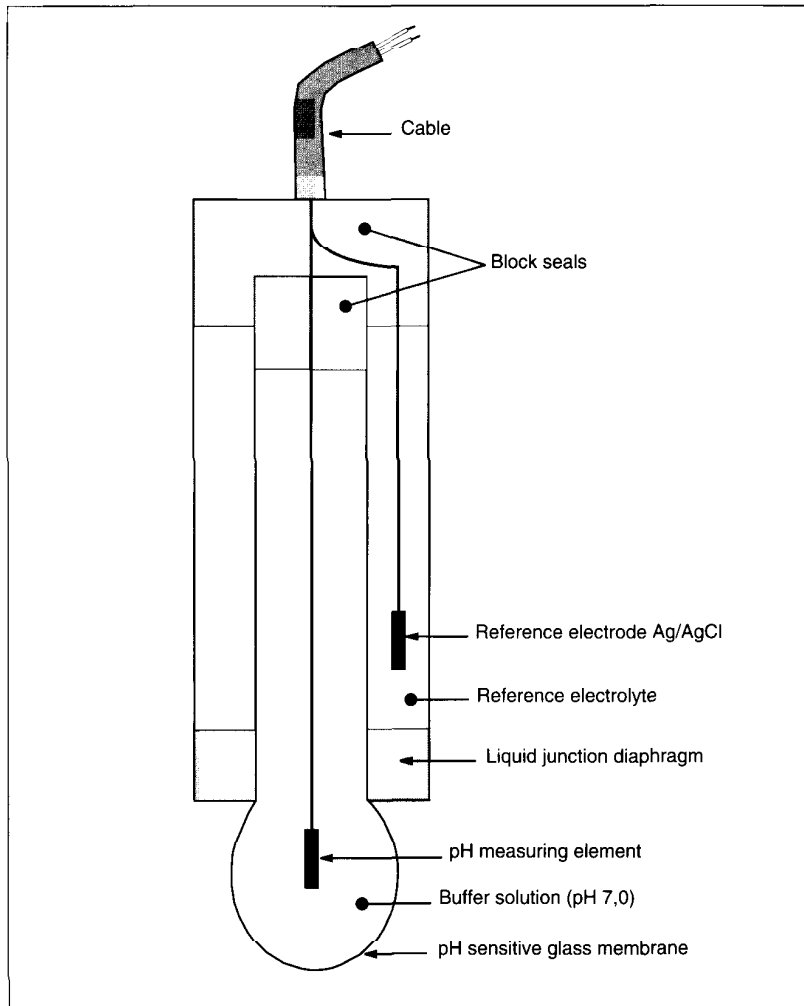
$$\text{Hence: } \text{pH} = -\log(1) = 0$$

In fact it is not possible to define the pH in this case.

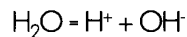
The problem has arisen because the presence of **WATER** is a requirement for the commonly used pH scale.

### Why is this so?

Water provides the interrelation between acidity and alkalinity through its property of splitting (dissociating) into an acidic part (hydrogen ions or protons) and an alkaline part (hydroxyl ions).



Overview of typical combination glass pH electrode



This dissociation is a precise process with a strict relation between the concentration of the partners:

$$[\text{H}^+] \cdot [\text{OH}^-] = 10^{-14}$$

With the aid of this relationship it is now possible to calculate the pH of a solution of a base e.g. NaOH that in the pure state has no protons.

E.g. a 1 mole/l NaOH solution (40 g/l) has a proton concentration of:

$$[\text{H}^+] = 10^{-14} / 1 = 10^{-14}$$

$$\text{Hence: } \text{pH} = -\log(10^{-14}) = 14$$

The equilibrium of water and its dissociation products: the proton and the hydroxyl ion always applies – to acid solutions as well as to alkaline ones. The magnitude of water's equilibrium constant means that the proton concentration is  $10^{-14}$  / (hydroxyl concentra-

tion) and vice versa, which is a large scale. Thus it makes sense to use logarithms which generate more easily handled numbers.

## 1.2 Measuring pH

There are many ways of determining the pH of solutions. Those in common use are pH test papers and instruments using the glass electrode pH sensor.

Test papers rely on the colour change when a dye changes from one form to another due to combination with or loss of a proton.

The glass electrode is an electrochemical device in which chemical energy is converted directly into an electrical signal. In particular a glass membrane made from a special glass which is pH sensitive generates a potential which depends on the pH

### The glass electrode

#### Components of the glass electrode

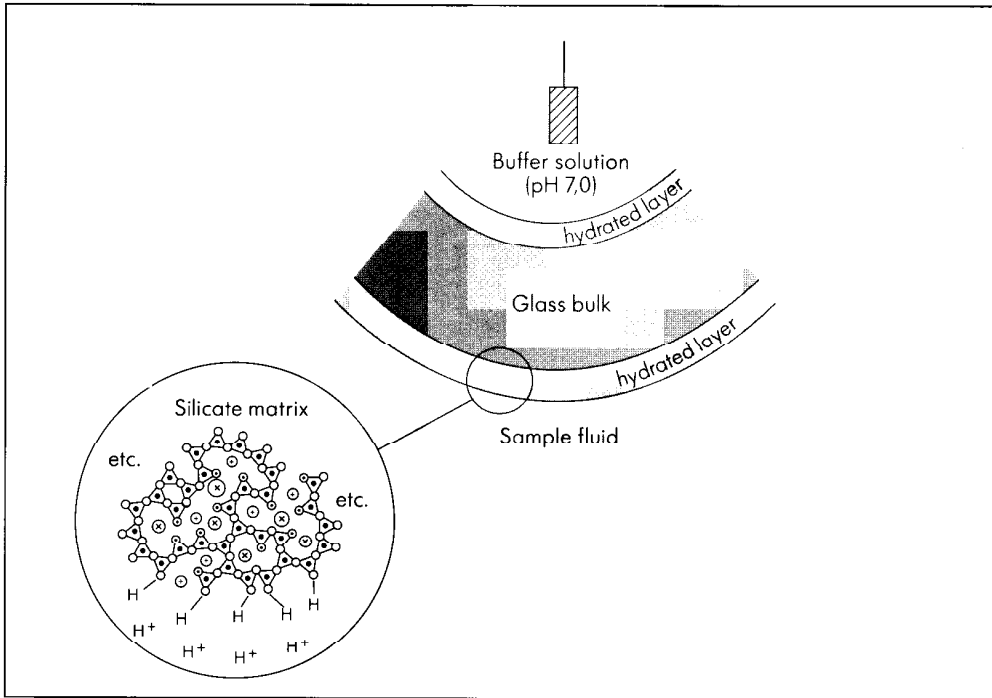
The pH measuring chain using the glass electrode is comprised of two so-called reference electrodes. These are the two connections to the pH meter and provide a stable conversion of the electrical signal in the connecting wires to the pH meter with the ionic (chemical) flow of electric charge which occurs in the solution. One reference electrode is immersed in a solution which gives a stable potential. This solution is separated from the sample solution by a porous diaphragm. The other electrode is immersed in a buffer solution of fixed pH. It is separated from the sample solution by the pH sensitive glass membrane.

In the SIGNET pH electrodes all of these components are combined in the same body. Such a form is called a combination electrode.

#### Operation of the glass electrode

The operation of the combination glass electrode is as follows. The pH sensitive glass is composed of silica oxide and an alkali metal oxide. Such a glass becomes hydrated in water – forming

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The operation of the pH sensitive glass

a gel layer, which contains many hydroxyl groups. These are sites that have an affinity for protons (i.e. hydrogen ion  $H^+$ ). The pH of the solution determines the degree of proton combination with the gel layer. The difference of proton activity in the solution bulk and in the gel layer results in a potential difference. This potential difference is dependent on the pH of the solution. This situation applies to both sides of the glass membrane, however, the filling of the glass electrode is a pH 7.0 buffer which remains constant, thus the potential difference at the inside surface is a constant. The glass electrode therefore gives a potential which is dependent on the pH of the external sample.

separate (i.e. not integrated into the pH sensor body).

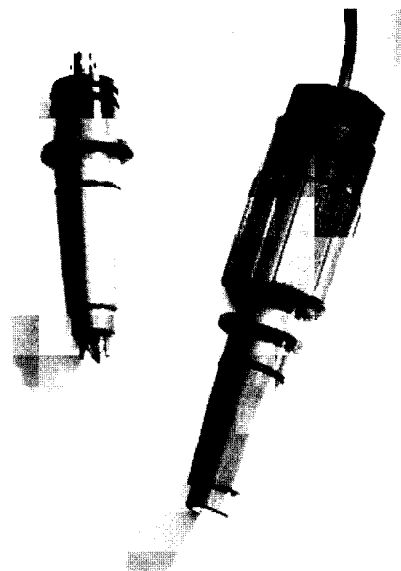
SICNET has simplified the whole concept of industrial pH measurement with a bold design concept:

- all sensors elements required for a temperature compensated pH measurement are contained in one single body (combination electrode)
- a pre-amplifier snaps directly on top of the electrode – eliminating problems inherent in high impedance signal lines (noise pick-up, moisture problems).

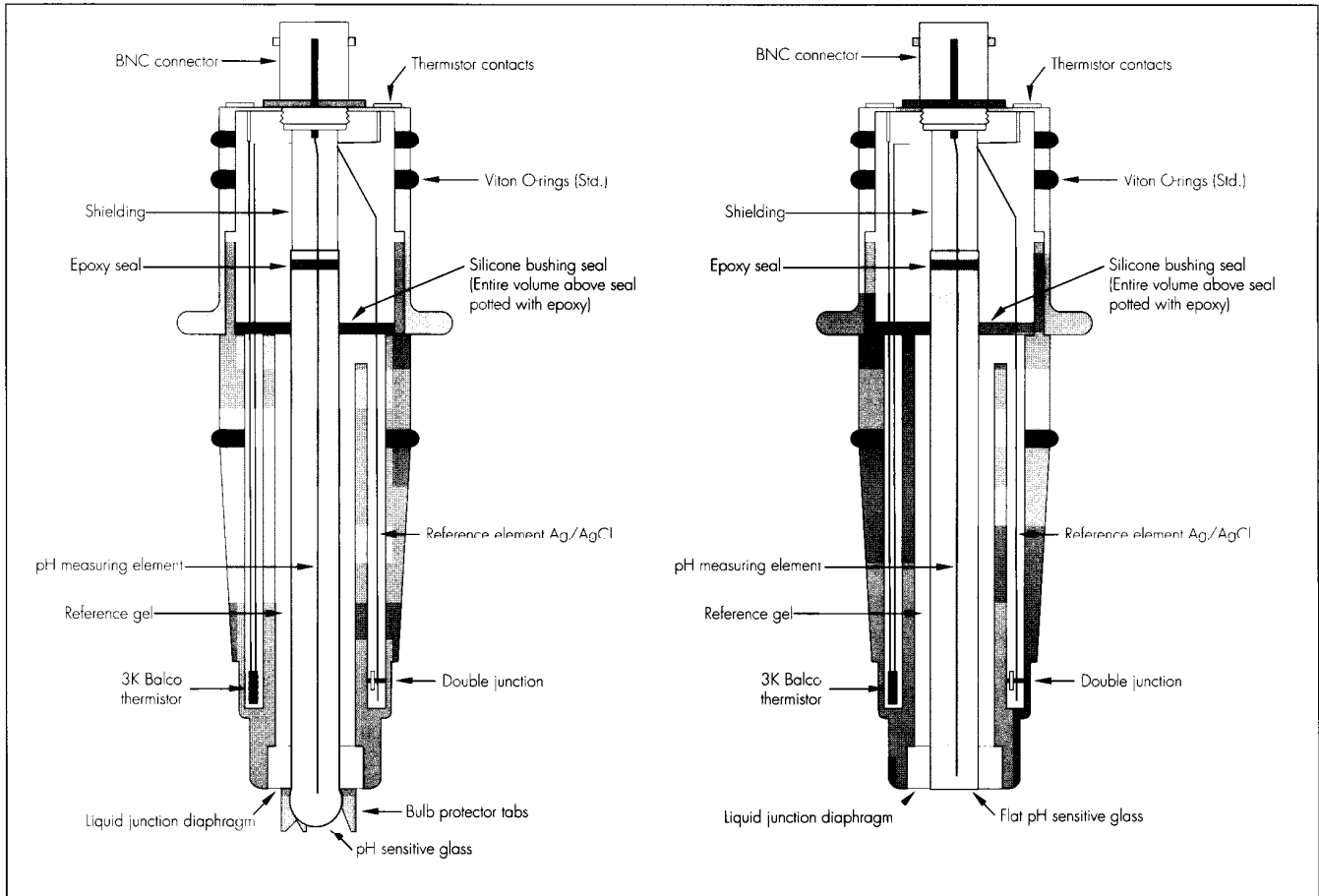
## Construction of SIGNET pH sensor

Glass electrodes used in laboratories are usually 12 mm diameter and 120 mm long. Most manufacturers of industrial pH measuring equipment make special (complex) adapters to accommodate these rather non-ideal sensor forms.

A temperature sensor is a separate item usually in the same format and often the reference electrode is also



Signet pH electrode and sensor

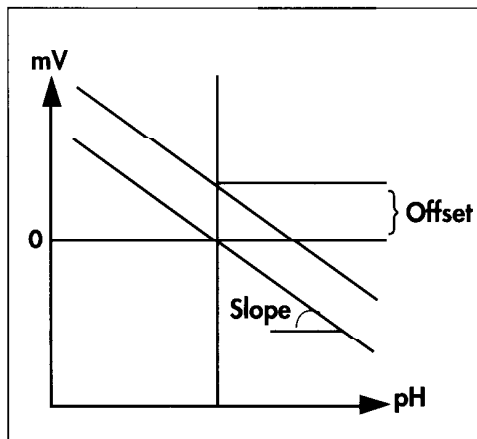


The SIGNET bulb and flat surface pH electrode construction

- the pH sensor is especially designed to be used in both submersible and in-line applications with the wide range of SIGNET fittings.

The SIGNET pH electrode is a compact unit (the so-called combination electrode). The parts exposed to the sample are the pH sensitive membrane of the glass electrode and the porous junction of the intermediate electrolyte bridge to the reference electrode. In the SIGNET electrodes this diaphragm is made out of porous UHMW Polyethylene.

The calibration curve of a pH sensor with offset and slope



The pH sensor is insensitive to most common problems in pH measurement, due to SIGNET's use of a double junction reference electrode and the flat pH sensitive glass electrode, which is recommended for particularly difficult sample systems.

## Calibration of the pH sensor

### The calibration parameters and their nominal values

As with most measurement systems the glass electrode requires two parameters to process its response. They are:

#### offset and slope.

The theoretical slope of the glass electrode is 59 mV per unit change of pH (at 25 °C). The 59 mV in fact varies slightly with temperature (see Appendix I for the reasons – Nernst equation).

The offset is the deviation of the electrode from the nominal value. All SIGNET pH electrodes ideally give an

output of 0 mV at pH 7. This has been selected by careful choice of the reference electrodes used and the composition of the solutions they are immersed into.

### Use of buffer solutions for determining the calibration parameters

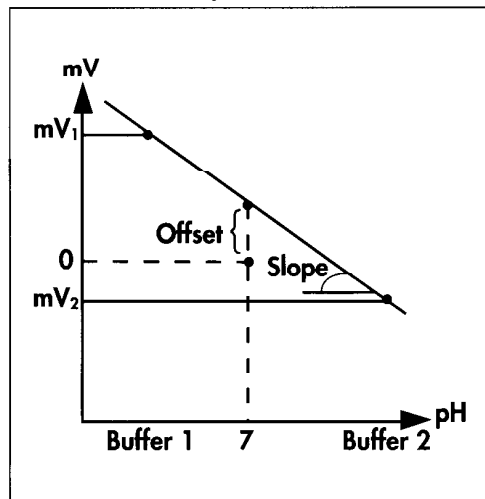
#### What are buffer solutions?

Buffer solutions are a mixture of at least two substances in water that through chemical equilibrium have the capacity to stabilise the pH of a solution at a particular value. The addition of caustic or acidic material to a buffer solution has an insignificant effect – so long as the amount added does not exceed the buffering capacity of the buffer solution.

Buffer solutions give a stable and reproducible pH value that facilitates exact calibration of the glass electrode.

The pH values of buffer solutions and their compositions have been normed world wide by the standardisation authorities (Appendix III).

#### The calibration procedure.



Two fixed points to determine the calibration parameters

The glass electrode should generally be calibrated with two buffer solutions having pH values at the ends of or within the pH range of the sample.

With the SIGNET analog instruments, the order in which the buffer solutions are used as well as the values taken are important if an iterative calibration procedure is to be avoided.

The first step is as follows: since the glass electrode has an output of nominally 0 mV at pH 7, the offset on the pH meter should first be set by dipping the glass electrode into a pH 7 buffer. With the zero point set, the slope can then be set using a buffer solution with a different pH value.

Using a microprocessor controlled pH meter, the calibration is much simpler in that the order of using the buffer solutions and the values they have are irrelevant.

#### What do the calibration parameters tell us?

The calibration parameters are not just determined to ensure an error free measurement. They also serve to indicate if the measurement is functioning correctly and if a failure is to be expected. Loss of slope or a sluggish response generally result from blockage of the junction or loss of sensitivity of the glass membrane. A shift of offset usually indicates depletion or contamination of the reference electrode. The frequency of the calibration and the point where maintenance or replacement of the sensor is required must be judged from the rate of drift and the expected errors resulting from such a drift rate between calibrations.

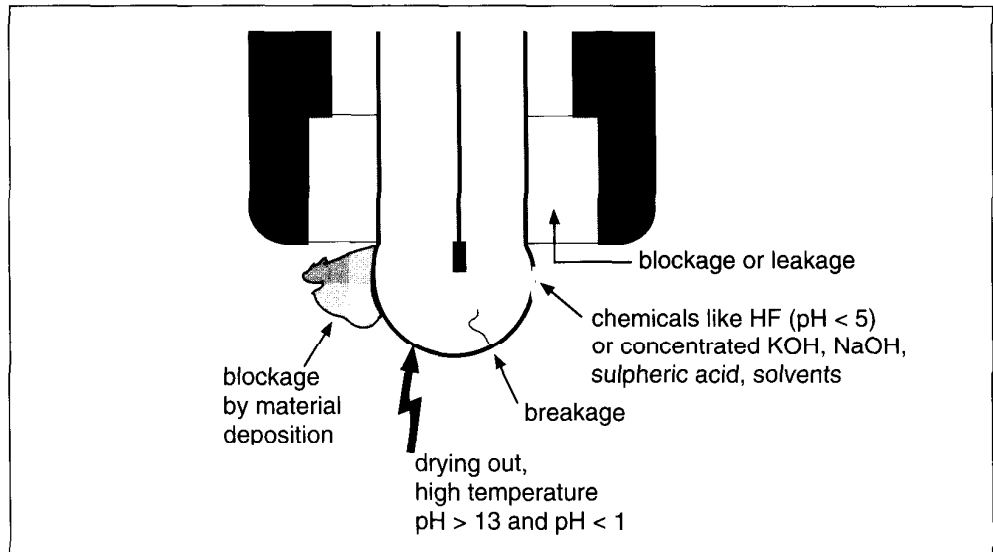
#### Difficulties in pH calibration

The buffer solutions used for calibrating the pH measurement are fairly concentrated (see Appendix III). Some applications, however, such as the measurement of the pH of drinking water or high purity water in power stations, have a sample that contains very little or no dissolved salts. The composition of the sample is therefore very different from that of the buffer solution.

This difference will lead to an offset error of the pH measurement. The error derives from the "diffusion potential" across the junction. This error is concentration dependent.

The error that can be expected depends on the concentration difference between sample and buffer solutions and in the worst case can amount to 0.2 – 0.3 pH units.

Typical sources of trouble with the pH sensor (electrode)



### Problems that can occur with the glass electrode.

Apart from the obvious failures that can occur e.g. breakage, there are a number of less obvious ones.

The sensitive parts of the glass electrode are:

- the reference electrode behind the junction
- the junction
- the glass membrane

The reference electrode can become contaminated with sample solution if transport of the sample through the junction occurs. This is normally unlikely but it is possible. The reference potential could thereby change, depending on the nature of the sample. Often the pH sensor can be used further if calibrated frequently.

(Note: such problems cannot occur with the measuring electrode behind the glass membrane since it does not allow any transport of solution.)

The reference junction is the weakest member of the pH measuring chain. It essentially connects the reference electrolyte to the process solution. The standard industrial silver/silver chloride reference electrode is immersed in a chloride containing solution. The reference junction enables these chloride ions to carry the current for the pH reference signal back to the process

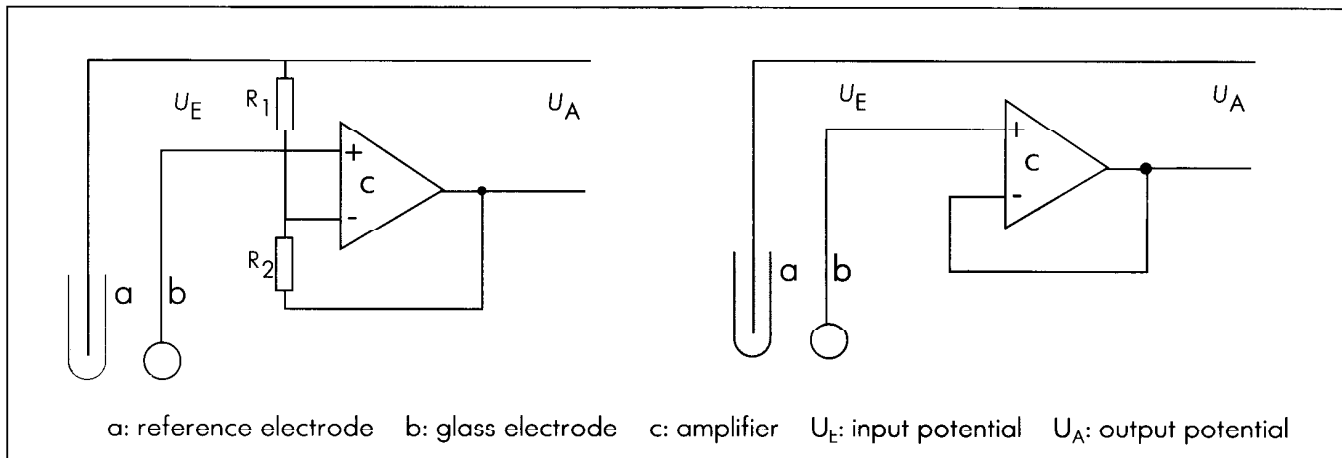
solution, thus completing the pH circuit. Unfortunately, this junction also enables the process solution to leach into the electrode, potentially contaminating the silver reference wire.

SIGNET pH sensors effectively eliminate this problem by using a double junction arrangement. The upper reference junction is not immersed directly in the process solution, but rather in a secondary, similar electrolyte, which acts as a filter for process ions which may contaminate or "poison" the electrode. Specific ions which cause notable, rapid deterioration to the silver reference wire include sulfides, bromide, iodide, cyanide, chlorine and ammonia. The long path, double junction design of the SIGNET electrodes provides significant protection against these elements.

The surface of the pH sensitive glass membrane must be gelled. It must always be moist so that the surface is hydrolyzed and responds to pH changes. Since the formation of this gel layer is slow (hours) it is important the glass electrode is always immersed in the sample or a storage solution.

(Note: The design of the sample lines and fittings in an industrial installation must ensure that this goal is achieved.)

Process streams may also contain substances that cause problems. Generally oils are detrimental to glass electrode performance. Biological liquids e.g. milk also can cause problems (protein deposition) as well as



Impedance conversion with pre-amplifier  
Right: with full feedback  
Left: with partial feedback

fluoride containing samples at low pH ( $\ll$  pH 5) which dissolve the glass! Any changes of the type mentioned above will lead to variations in the calibration parameters or worse – loss of the pH measurement capability completely.

to install a pH sensor in such way that is ideal for the pH measurement. Equipment design and process conditions are given and to properly install the measurement the best location has to be found. The best pH values are measured when all the basic installation guidelines are respected.

### 1.3 Requirements of the glass electrode on the measurement electronics

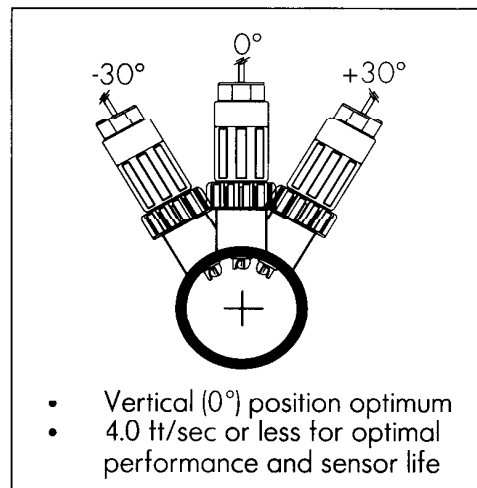
The membrane of the glass electrode is in principle an isolator. The chemical composition of the glass has, however, been selected to give a minimal resistance. Nevertheless, the resistance across the glass membrane is between 100 and 1000 M-Ohm (depending on the temperature).

It is clear therefore that an amplifier with very high input impedance and low input bias current is required. In SIGNET pH sensors this high impedance signal is converted to a low impedance one with a pre-amplifier mounted directly in the sensor head.

The advantage is that there is no need for special high quality screened (or double screened) cables between the pH sensor and the instrument or controller which most competitors products require.

- The pH electrode must be in solution at all times.
- The pH electrode must be installed vertically ( $\pm 30^\circ$ )
- Flow rate past the pH sensor should be less than 4 ft/sec for the standard pH electrode (less than 5 ft/sec for the flat surface pH electrode).
- The pH sensor should be placed in a position that reflects the pH of the total process fluid. Hence, good mixing of the process fluid is essential.
- The installation must provide an easy removal of the pH sensor from the process for cleaning and calibration purposes (e.g. installation in a by-pass).

### 1.4 Typical pH sensor installation guidelines



In process equipment often it is difficult

Mounting position of a pH sensor

## 1.5 Typical maintenance of pH sensors

pH electrodes are subject to an altering process. Temperature, sample and process conditions are influencing the life time and maintenance of a pH electrode.

### Cleaning

A pH electrode should be cleaned on a regular basis (ideally before each calibration). Both the glass and reference diaphragm must be cleaned.

For a standard water or waste water application it is recommended to rinse the electrode with tap-water and to immerse it several times in a 5 % HCl solution to remove hard water deposits from the diaphragm. To remove mild grease or oil deposits from the surface of the glass membrane the electrode might be wiped gently in isopropyl alcohol.

### Calibration

Calibration of the pH electrode has to be performed every 2–8 weeks depending on the application.

### Electrode replacement

The average pH electrode replacement is every 1–2 years. Some last longer and some last shorter.

## 1.6 Some typical applications of pH measurement

pH measurement is the most common example of the measurement of the concentration of a specific chemical species. This is not surprising since pH effects a multitude of processes:

- corrosion rates
- precipitation of heavy metals
- activity of oxidizing/reducing agents
- biological activity

In fact in most processes involving aqueous solutions of chemicals, the pH plays some role. There are many examples to be found in the industry, environmental control, utilities, etc. to determine product quality, to enhance

production efficiency and to assure environmental- or product safety.

### Electroplating, Surface finishing

- etching and pickling bath control
- plating bath control
- pH control in chromate and cyanide destruction

### Waste water (sewage) treatment

- precipitation of heavy metals (at high pH)
- neutralization

### Clear water treatment

- drinking water
- swimming pools
- boiler feed water
- cooling towers

### Process control

- sugar refining
- photo developing
- photo emulsion manufacturing
- flue gas scrubbing

## 1.7 Not recommended applications

In the chemical and biochemical industry there are certain process monitoring applications for pH sensors, that demand highly specialized systems e.g.:

- high temperatures and pressures
- additional cleaning aids
- EEx proof for use in hazardous areas
- in-line calibration or cleaning requirements
- steam sterilizable
- pH measurements continuous between 0 and 2 or 12 and 14

These are low volume, specialized niche markets which can be troublesome.

The SIGNET general purpose sensor concept for submersible and in-line use, covers a large number of applications.

## 1.8 SIGNET pH instrumentation

George Fischer offers a line of flexible pH measurement systems to suit a large number of applications. Ranging from the simple to operate, 2-wire loop powered 4-20 mA transmitter model SIGNET 8710 to the SIGNET 9030 Inteltek-Pro pH controller.

The latter is a microprocessor controlled instrument which can be configured with additional plug-in cards to provide extra functions (relays, controller outputs, analog outputs). It accepts all SIGNET pH sensors signals— including 4–20 mA signals. All input cards have galvanically separated inputs to ensure that ground problems do not occur.

pH measurements are even simpler with the SIGNET 8710 pH transmitter featuring push-button programming and a versatile, simple to mount enclosure. The microprocessor-based digital electronics sealed in a NEMA 4X (IP65) housing allows a calibration in a few minutes.

Both the SIGNET 9030 Inteltek-Pro pH controller and SIGNET 8710 pH Transmitter are combined with the SIGNET pH sensor system.

### SIGNET "Twist-Lock" pH Sensor System

George Fischer specializes in providing



SIGNET "Twist-Lock" pH electrode replacement system

simple, affordable solutions to fluid monitoring and control. The SIGNET pH sensor system is a prime example of this commitment.

The SIGNET 2714 and 2716 pH Electrodes feature a combination design with measurement, reference, and temperature compensation element in one virtually unbreakable plastic body.

Amplification is done with the SIGNET 2720 Pre-amplifier which snaps directly on top of the electrode for superior signal quality in virtually any application. The unique "twist-lock" connection design makes removal and replacement of the electrodes so simple it can be done in seconds.

### Key Specifications

SIGNET 8710 pH Transmitter

- Loop power: DC 10 to 30 V
- Current output: 4 to 20 mA (adjustable)
- pH range: 0 to 14
- Display accuracy:  $\pm 0.03$  pH
- Enclosure rating: NEMA 4X (IP65)

SIGNET 9030 pH Controller

- Power supply: AC 90 to 132 or 180 to 264 V and DC 16 to 30 V
- Current output: 4 to 20 mA
- Alarms: 2 SPDT contacts, Max. 5 A at AC 250 V
- Dual proportional output: 2 SPST contacts, Max. 5 A at AC 250 V
- pH Range: 0 to 14
- Display accuracy:  $\pm 0.02$  pH
- Enclosure: 1/4 DIN (96x96)
- Enclosure rating (front only): NEMA 4X (IP65)

SIGNET 2720 Pre-amplifier

- Housing material: CPVC
- Gain: X1 (Unity)
- Operating temperature: 0 to 80°C
- Submersible: NEMA 6P (IP68)

SIGNET 2714/2716 pH electrodes

- Range: 0 to 14 pH
- Sensor body: CPVC
- O-rings: Viton®
- Reference electrode: Ag/AgCl double junction
- Junction Material: Porous UHMW Polyethylene
- Max. process pressure/temperature: 7 bar max. at 65°C  
4 bar max. at 85°C

## 1.9 pH Control

Control is the process of keeping a particular property at a desired set-point. In pH control, it is the pH which is controlled, it is done by adding an alkaline substance to raise the pH or an acidic one to lower the pH of the sample. The amount of substance which must be added is determined by the response curve of the system. For pH control, the pH of the acid or alkali concentration is dependent.

We have shown in Section 1.1. that pH is a logarithmic function. With each single step change in pH, the concentration of  $H^+$  ion changes by a factor of 10. For this reason, pH control is quite difficult, and whenever possible, it is recommended that the control be done in a tank. pH adjustment of no more than 3 pH units in a single tank is also advised, as the delivery system of the reagent generally can not do better than the 100 to 1 difference in demand for the three pH steps (i.e., 100 x for third step, 10 x for second step, 1 x for first step). A well mixed system for introducing the reagent is also highly recommended. Generally, an impeller type mixer does significantly better mixing than either a recirculated pumped system or air sparging.

An additional complication which is common to many industrial control situations is the existence of a time delay between adding chemicals and measuring any response.

### The error signal

The difference between the system pH and the required pH is the error signal. The error signal controls the amount of chemicals to be added to the system

being controlled. It is translated by the SIGNET Proportional Controller into a control signal for the chemicals dispensing.

### The pH response curve

The logarithmic nature of pH is also revealed in the pH response curves generated when a reagent is added to a solution. Depending on the strength of the acids and bases involved, the response curve will vary. A weak acid neutralized by a weak base shows a much flatter response curve. If mixtures (or acids with several stages of dissociation) are neutralized, the response curve shows several steps.

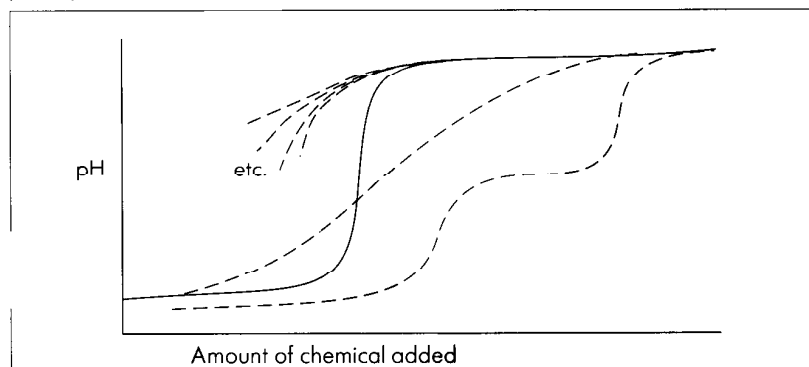
This means that no general formula can be applied to determining the control parameters. In the absence of a sophisticated adaptive algorithm, the controller must be optimized individually for the particular chemistry at hand.

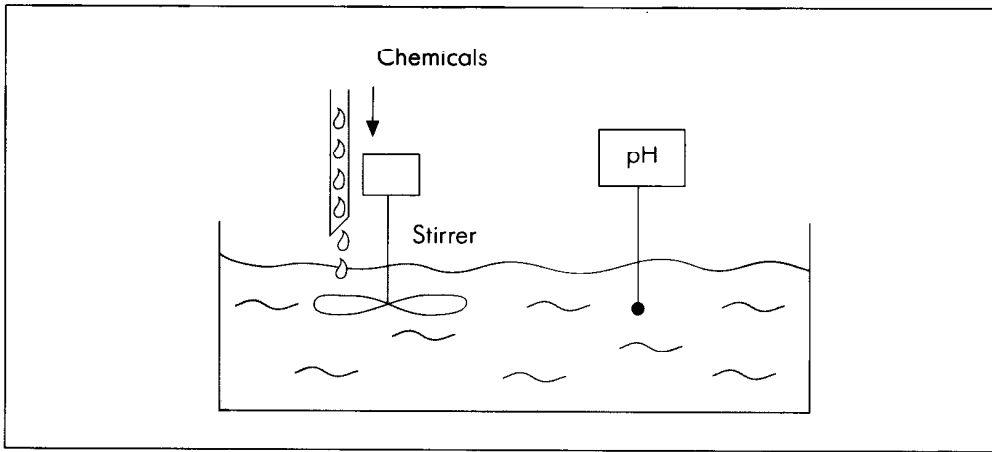
### Controllers

The nature of the pH controller depends in large measure on whether On-Off or proportional control is employed. The principal component in On-Off control is the alarm, a relay which can change state as the pH changes across a predetermined value. The relay turns a solenoid valve on and off, dispensing basic reagent into the process fluid when required, as the pH of the mixture varies below and above the chosen value.

For a proportional control system, determine if a pump or a valve is to be used as the control element. A proportional pulse or proportional 4-20 mA signal from a proportional controller should be used depending on the requirements of that specific pump or valve. As the pH value of the process approaches the set-point the control signal linearly decreases the dispensing of chemicals. At zero error there is no dispensing of chemicals. As the system drifts away from the set-point the control signal increases slowly.

pH response curves





**Example 1:**  
 If a stirred tank is used, the chemicals dosing should be close to the stirrer. The pH sensor should also be in a well stirred region but not close to the chemicals addition point.

The SIGNET Intelek-Pro controllers have both capabilities, ON-OFF control and proportional control. Both methods are used for control of pH in a tank. On-off control is generally less expensive in terms of the delivery system (pumps/valves) involved, but may cause overuse of the neutralizing reagent. Proportional control provides the advantage of slowing down the delivery of the reagent to the tank as the set-point is approached, and prevents overshooting the set point and wasting of reagent.

For more complex process control, or if in-line control is necessary, a PI or PID controller should be used. In these applications, it is recommended to use the SIGNET 8710 pH transmitter and 2720/2714 sensor system to monitor the pH, provide simple calibration, and transmit the signal to the PI/PID controller.

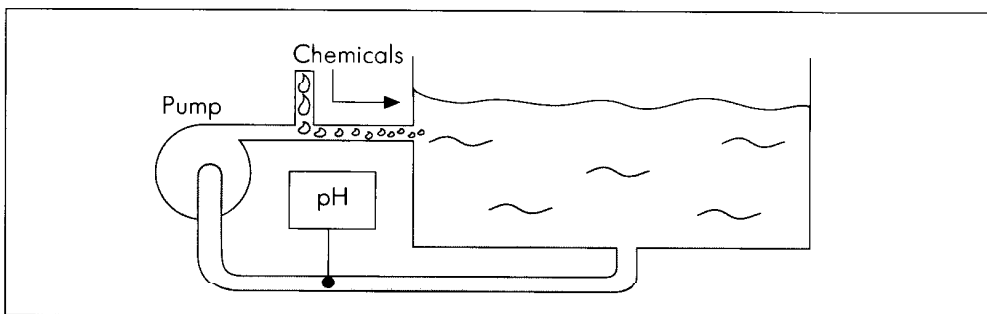
### Some pH control applications

#### Example 1:

This is a standard application of neutralization in a stirred tank. It is recommended that the waste and the reagent enter the tank on one side, while the sensor is located on the opposite side of the tank, near the point of discharge.

#### Example 2:

This is a situation where chemicals are added in a sample pipeline in which the sample is recycled to a large hold-up tank – e.g. typical of a swimming pool application. Don't place the pH sensor after the chemicals addition – even if there is a good stirring of sample and reagent. This will effectively control the pH of the sample being returned to the hold-up tank. However, it is not a good control strategy for the total sample in the hold-up tank since an infinite time will be required to reach the set-point.



**Example 2:**  
 In this case place the pH sensor before the chemicals addition to measure the pH of the sample in the hold-up tank

### Example 3:

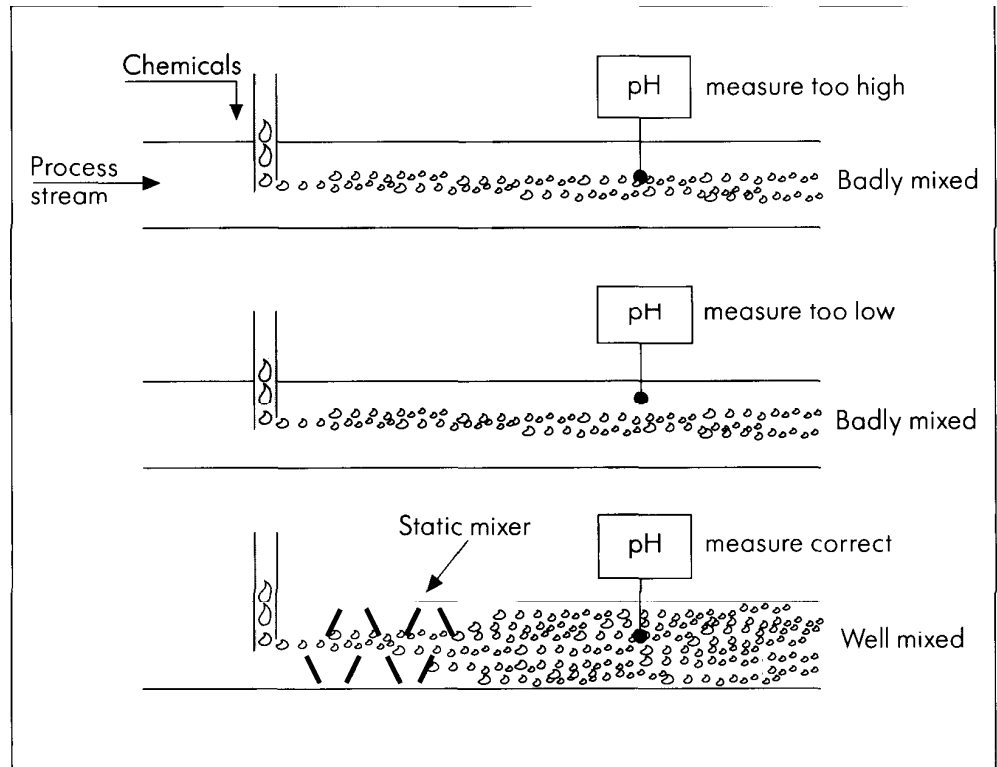
This application shows a sample pipeline with the pH sensor placed downstream from the chemical addition point (feedback control). As stated earlier, if in-line control is required, a PI or PID controller will be necessary. If reagent is added prior to the sensor, a static mixer to ensure adequate mixing of the solution should be used. For in-line monitoring only, any SIGNET system could be used. For all in-line applications, velocity in the pipe should be kept at less than 4 ft/sec when a bulb electrode is being used, or less than 5 ft/sec when a flat surface electrode is being used.

### Summary of pH control

The positioning of stirrer, pH sensor and point of introduction of the chemicals is critical!

- The chemicals should be mixed as effectively as possible with the process water.
- The pH sensor should be placed in a position that reflects the pH of the total process water.

Example 3:  
Don't place a pH sensor downstream from a chemicals dosing point in a sample pipeline unless the mixing of chemicals is complete. The system may just measure the chemicals or only the sample and be impossible to control



## 2. ORP measurements

Unlike the pH measurement, the ORP measurement is not specific for a particular substance. Instead it is a measure of the oxidising or reducing power of the sample. This measurement is an example of an electrochemical one, i.e. the direct inter-conversion of a charge transfer process in an electrical conductor – electrons, with that in a solution – ions. The electrode required to effect this simple process is a metal. The metal selected must, however, be inert. Usually platinum is selected since it is only attacked by a few very aggressive acids.

The simplest example of a ORP measurement is in a solution containing iron salts in the two forms ferrous and ferric.

The only difference between the two forms is that the ferrous form has one electron more than the ferric form. When the platinum electrode is immersed in such a solution and a potential applied between it and a reference electrode, it is possible to generate a current flow in which either electrons are forced to flow to the ions in the solution and add on to the ferric ions thus reducing them or vice versa, i.e. if a more positive potential is applied, electrons will be taken from the ferrous ions in solution thus causing their oxidation.

At a precisely defined potential, which can be calculated from the Nernst equation, the net transfer of electrons from the platinum wire to the solution is zero. (At this potential the transfer of electrons is not "frozen" but rather the forward rate is equal to the backward transfer rate – these individual rates are called the exchange current densities). This potential is the characteristic ORP (Redox) potential of the solution.

The ORP sensor simply measures potential and since it is a high impedance device it takes (or gives) no current to the electrode. Thus the chemical system stays in its natural equilibrium

It is seen from the Nernst equation that

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the ORP potential is concentration dependent – thus it is often used as a measure of the concentration of oxidizing agents (less often reducing agents)

### 2.1 The ORP scale

Chemical processes are typified by relatively low potentials, when compared to the standard 110/230 V domestic power supply. It is perhaps surprising that the most powerful oxidation or reductions are associated with potentials in the range -3 to +3 V. The strongest oxidising agent is fluorine and the strongest reducing agent is lithium.

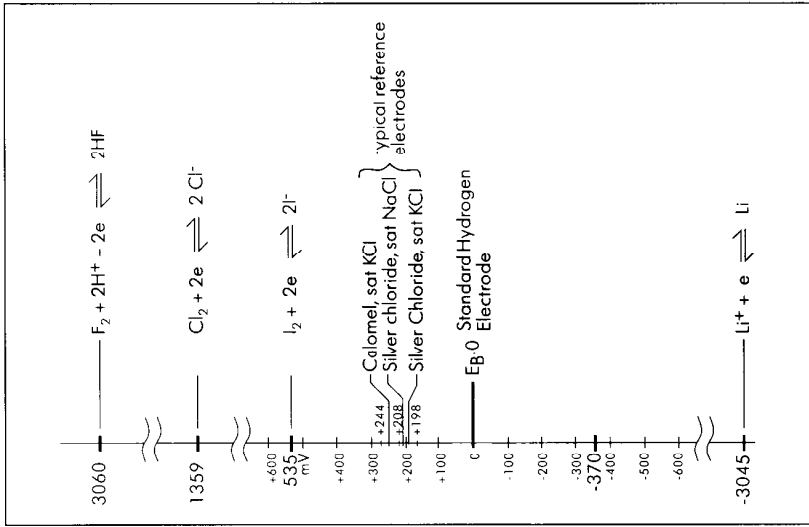
The ORP of some common systems together with the extremes are given in Appendix III.

All ORP potentials are standardized against the "hydrogen electrode". This is the international standard reference electrode and has the potential zero. However, it is not a very practical electrode to work with. Therefore, ORP's (as well as other electrochemical potentials) are usually quoted with respect to a common reference electrode like the one used in SIGNET ORP sensor: the silver/silver chloride electrode. The silver/silver chloride electrode has a potential +0.198V against the hydrogen electrode. This means that potentials measured with the silver/silver chloride electrode will be 0.198V more negative than those expected on the basis of the table in Appendix III.

### 2.2 Restriction on the analytical significance of ORP measurements

#### What does ORP actually mean?

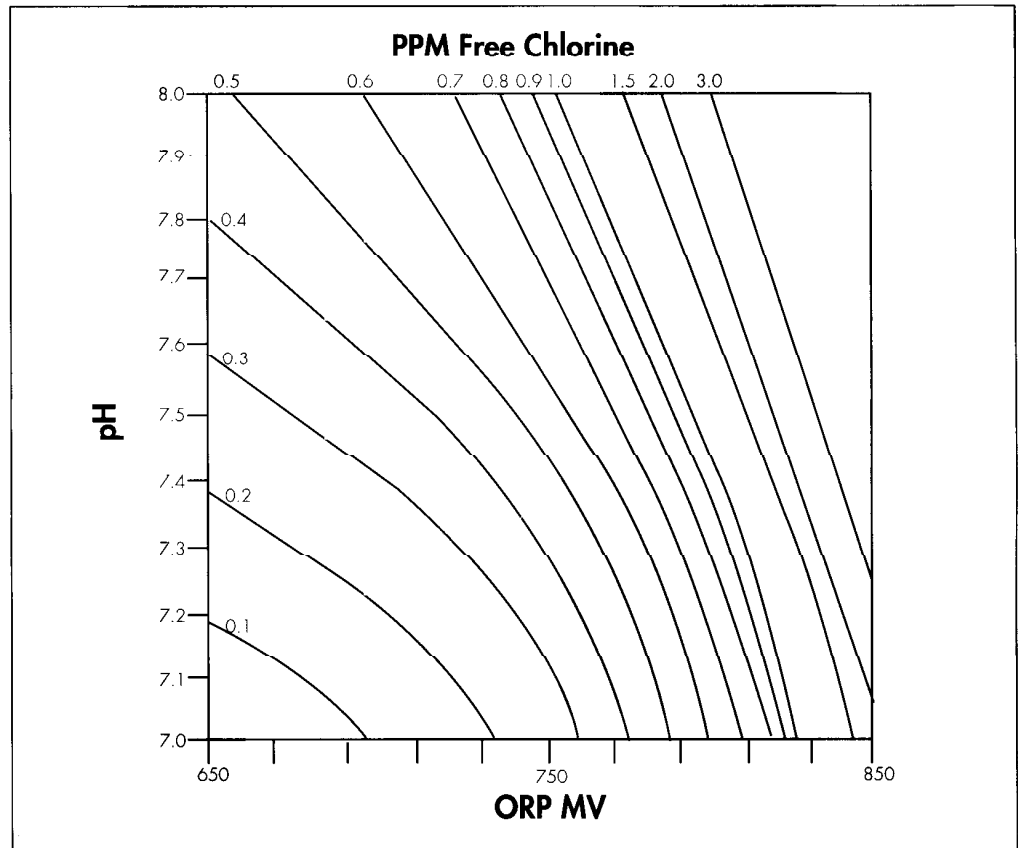
As mentioned previously the ORP is a measure of the oxidizing or reducing power of a solution. Since some oxidizers (or reducers) are much stronger than others, the measurement is not a measurement of concentration (total) of all oxidizing (or reducing) species, but more importantly, a measure of the total oxidizing capability (power or potential) that the solution has.



Some oxidizing/reducing systems

As the measured value of ORP increases, the solution has more potential to oxidize. One good example of an oxidation process is the monitoring of swimming pool disinfectants. As we increase the amount of disinfectant (generally chlorine) into the pool, the ORP increases. With the higher value of ORP, our pool water is more active - has more potential to destroy any organisms, and does this destruction more quickly. As the chlorine is consumed, the ORP drops again, signaling to the controller to replenish the chlorine into the water.

Variation of ORP for free chlorine as a function of pH.



## ORP vs. PPM Chlorine

Correlating the ORP to an exact concentration of chlorine in water is often desired, but is not so straightforward. There are two causes for this. First, the activity of the chlorine in the water is greatly affected by the pH. This is caused by a conversion of the form of chlorine in the water from hypochlorous acid (HOCl) to hypochlorous ion (OCl<sup>-</sup>) as the pH increases. Unfortunately, the latter, hypochlorous ion is 80 to 300 times less effective than the hypochlorous acid. The lower oxidizing activity of this form of the chlorine results in a lower oxidation potential, or ORP. It is therefore critical to know the exact pH (or better yet, control the pH) in order to make a correlation to PPM chlorine. The figure below shows the relationship between pH, ORP and ppm chlorine for various conditions frequently used in disinfection.

The second cause of difficulty requires re-examination of the Nernst equation. This shows us that the ORP measurement is made up of the ratio of at least two concentrations.

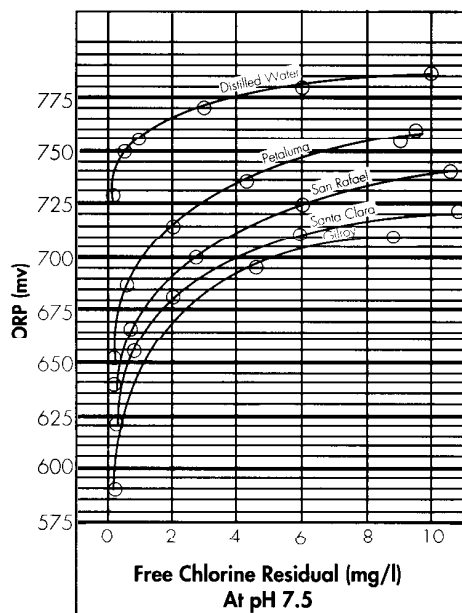
$$E = E^0 + (RT/nF) \ln (a_{ox}/a_{red})$$

These are the concentrations of the oxidizing agent and its reduced form or reducing agent and its oxidized form.

In the case of the common oxidizing agent chlorine, the reduced form is the unreactive chloride (as in common table salt). Since the ORP is proportional to the ratio of these concentrations (affecting the equilibrium state of the reaction), a greater concentration of chlorides in the solution will also cause the ORP to decrease. This is illustrated quite well by some work done in California, examining the differences in ORP for different waters at constant pH (7.5), and varying levels of chlorine (See figure below). As the salt in the water (chloride) increases, oxidation potential (ORP) decreases.

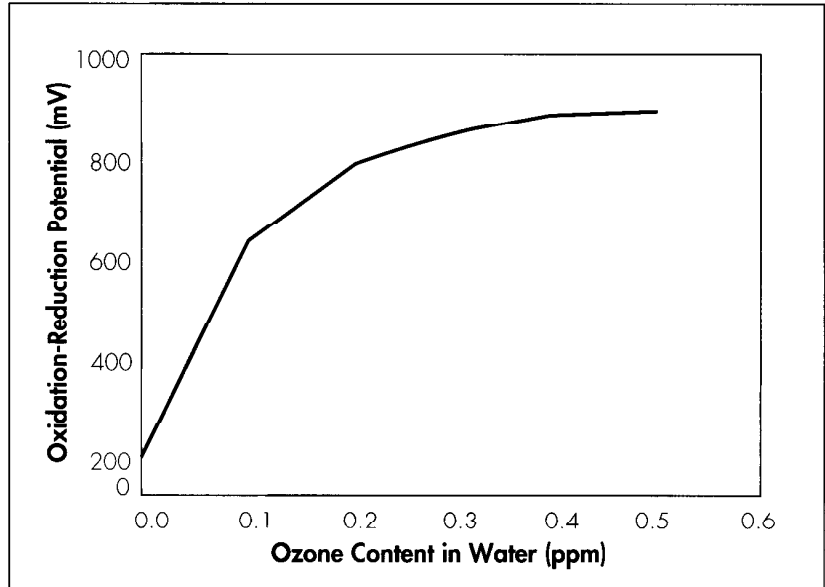
If the salt level in any water remains fairly constant, the appropriate relationship can be derived, and a set point selected to enable the chlorine concentration to be maintained for any given level of pH. It should be reinforced however, that only ORP represents the true oxidizing capability of the solution, while a measurement of ppm chlorine may represent chlorine present in a very inactive oxidation state.

Relationship between oxidation potential and free chlorine residual at a constant pH in five different waters.



### ORP and Ozone

Measurement of ozone in water with ORP is much more straightforward than the measurement of chlorine. The primary reason for this is that the ozone does not change its form in the water (combine with other molecules), and therefore is not affected by pH. The relationship between ORP and ozone is shown in figure below. This measurement has found important applications in aquariums, bottled drinking water, and other disinfection applications.



## 2.3 SIGNET ORP sensor Construction

The SIGNET ORP sensor has a similar construction to the pH sensor – except of course that instead of a glass electrode, the much simpler ORP electrode in the form of a platinum band is employed.

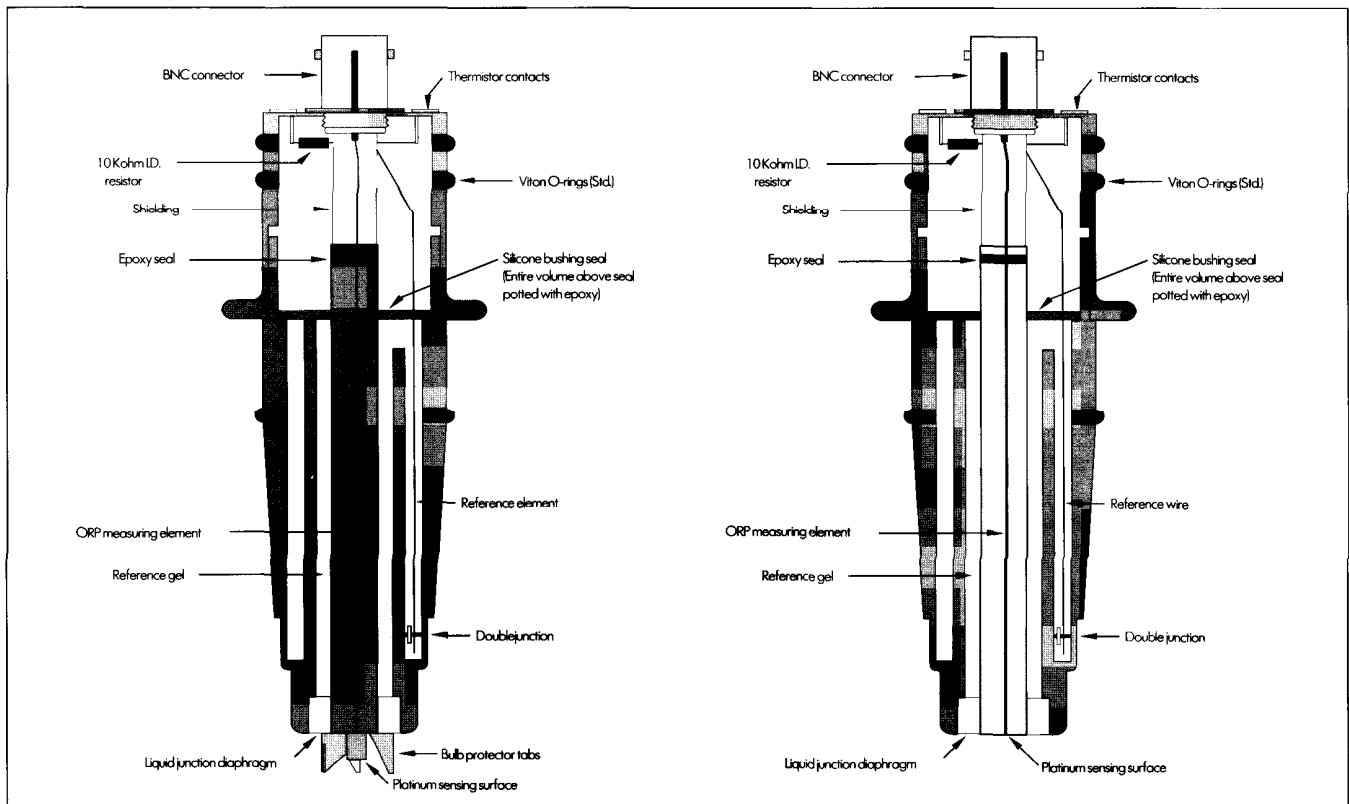
The same pre-amplifier is used as in the pH sensor. Although the ORP sensor is a fairly low impedance device, the pre-amplifier ensures that no current is drawn through the platinum electrode and that the measurement is not invalidated by "polarization" effects. (Note: Polarization is the effect of the electrode potential shifting when current is drawn. An electrode is like a resistance: a potential difference is required for a current to flow. Reference electrodes – whose duty is to provide a stable potential – are constructed with very low impedance and are virtually non-polarizable. That is current can be drawn with little potential shift.)

## Calibration of the ORP electrode

Regular calibration of the ORP electrode is necessary to compensate for any standard and slope drift. A monthly frequency is typical in many disinfection applications. Verification is best accomplished in freshly made solutions of quihydrone saturated pH 4.0 and pH 7.0 buffer solutions.

Quihydrone is a weak reducing agent whose activity changes with the pH. By adding it to solutions of known pH, standard ORP solutions of 87 mV (pH 7.0 buffer) and 264 mV (pH 4.0 buffer) are obtained. These standard solutions are used to monitor the standard and slope of the ORP sensor. A shift in the standard or slope generally occurs from depletion of the reference side of the electrode. A decrease in span between the two points is generally caused by contamination of the platinum electrode surface. A good cleaning of the probe might help to restore these values, otherwise the electrode should be replaced.

The SIGNET bulb and flat surface ORP electrodes



## Problems that can occur with the ORP electrode.

The problems that can occur with the ORP measurement are similar to those with the pH sensor. Apart from the obvious problems such as blockage of the electrode with isolating oils, fat or other deposits can cause, it is usually the reference electrode with the sensitive junctions that is the major source of trouble. However, due to the SIGNET double junction reference electrode, such problems are kept to a minimum.

Different from the glass electrode for pH measurement, the ORP electrode is a low impedance device. The measuring electrode comes directly in contact with the sample. The highest impedance element in the measurement is the junction of the reference electrode.

## 2.4 Some typical applications of ORP measurement

ORP measurements find applications in water monitoring after a disinfection step – e.g. addition of chlorine, dioxide or ozone.

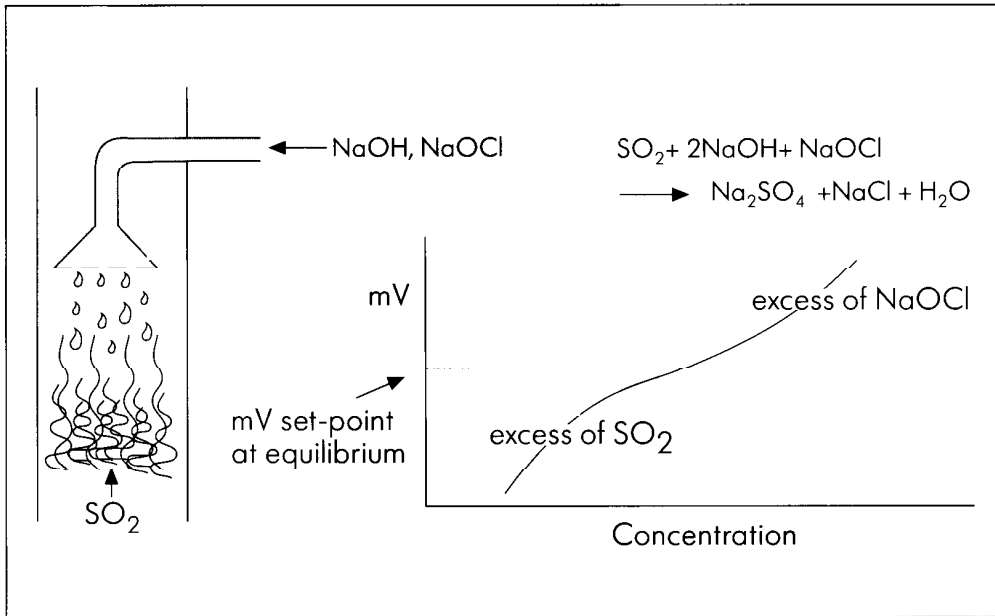
Such process are employed in:

- swimming pools
- potable water treatment
- ultra-pure water (semi-conductor)
- sterile process water (pharmaceutical)

Other common applications are in flue gas scrubbers e.g. for the oxidation of sulfur dioxide or the destruction of cyanides.

## 2.5 SIGNET ORP instrumentation

George Fischer offers a line of flexible ORP measurement systems to suit a large number of applications. The construction, features, and most of the specifications are identical to the pH measurement systems described in chapter 1.8.



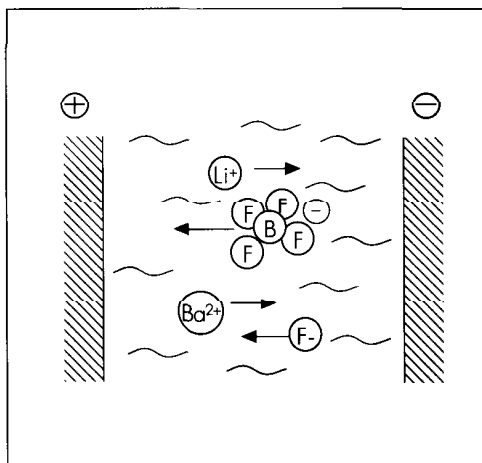
Flue gas scrubber application

### 3. Conductivity measurements

#### 3.1 Properties of electrolytic conductivity

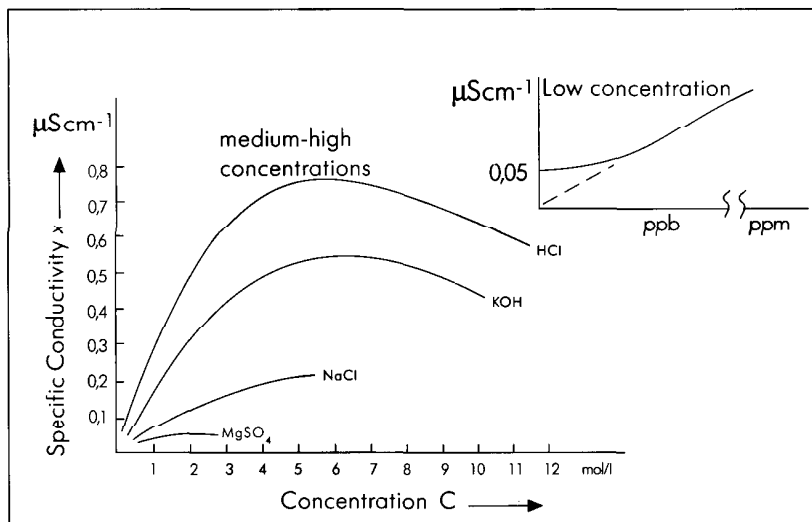
As we have seen, the measurement of pH and ORP potential are electrochemical methods (i.e. methods which are based on the flow of electricity but in a solution containing an ionic conductor. A basic property of the solution for electrochemical measurements is the conductivity itself whereby all dissolved ionic species add to the conductivity of the solution.

Ionic conductivity



The conductivity measurement is not surprising the least specific of electrochemical measurements, but is not necessarily an obstacle in its application in an industrial control task.

Conductivity as a function of concentration and substance



The classic example is the monitoring and control of a de-salination plant. Here the function of the plant is to remove all dissolved ionic species from the sample. This is the most common application. Often, however, conductivity is used to estimate the concentration of a dissolved ionic species.

As can be appreciated from the non-selectivity of the conductivity measurement this can only be possible when the process solution has a very simple composition (best a pure substance) and the concentration varies over a small range.

#### Properties of electrolytic conductivity

In contrast to electronic conduction in a copper wire, electrolytic conductivity has more parameters that effect the conduction process:

- there is a difference between a conductivity measurement with AC and DC
- the conductivity is dependent on the solvent, nature of the ions dissolved and temperature
- the concentration dependence is non-linear in very dilute (pure) solutions and in concentrated solutions
- the conductivity is dependent on chemical equilibria, i.e. conducting ions can combine to give less conducting ions

We shall see in the next sections the reasons for these phenomena.

### 3.2 Conductivity units

There are three units of measurement commonly used to express conductivity. They are:

**Siemens/cm mhos/cm and Ohm•cm**

where Siemens/cm is exactly equal to mhos/cm, and both represent the inverse of Ohm•cm. In the U.S., the Siemens/cm and mhos/cm are the preferred measurement units. The unit of Siemens was set by the International Standards Organization to replace the unit of mhos, but both continue to remain popular today.

The conductivity range found in most water supplies, (not pure water), is in the magnitude of 1/1000 of the Siemen, and is therefore designated as it's metric equivalent, the microSiemen/cm ( $\mu\text{S/cm}$ ) or micromho/cm ( $\mu\text{mho/cm}$ ). Readings are standardized to a 1.0 cm cell constant, and it is common to see the cm<sup>-1</sup> unit dropped from the term. Although the unit is not mentioned, it is always assumed to be present.

The unit of Ohm•cm is used in applications of resistivity, especially for the monitoring of high purity water. In these cases, the magnitude of the reading is in the million of Ohms•cm, and is converted to it's metric equivalent, the Meg Ohm ( $\text{M}\Omega$ ), with the •cm assumed.

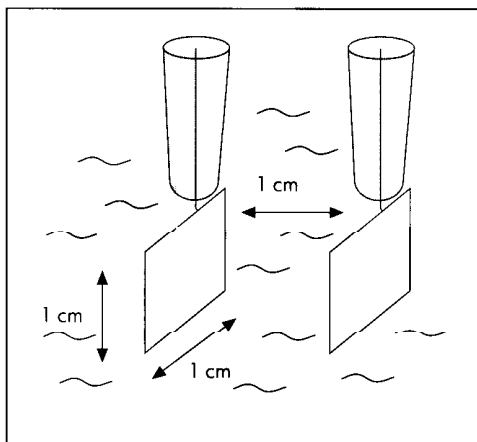
In all cases, the definition of the unit is based on the resistance of the sample measured between two parallel square plates of 1 cm<sup>2</sup> area placed 1 cm apart.

inserted in the equations above. The characteristic property of the measuring cell is the

$$\text{cell constant} = \frac{\text{electrode separation}}{\text{electrode area}}$$

and has the units cm<sup>-1</sup>. Usually the cell constant is determined by the manufacturer and defined in the product specification – even for complex geometries.

Most applications of conductivity measurement occur with aqueous systems. The range of conductivity typically covers the range of 1  $\mu\text{S}$  to 1,000,000  $\mu\text{S}$  (1,000,000  $\mu\text{S}$  = 1,000 mS = 1S). Some commonly encountered samples are given in Appendix III.4.



Classical 1 cm<sup>3</sup> measuring cell

$$\text{Measured resistance} = \frac{\text{resistivity} \times \text{electrode separation}}{\text{electrode area}}$$

$$\text{Measured conductance} = \frac{\text{conductivity} \times \text{electrode area}}{\text{electrode separation}}$$

$$\text{Conductivity} = 1 / \text{resistivity}$$

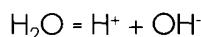
In practical industrial measurement systems the parallel plate measuring cell used in the definition is rarely used. However, this is not important since the particular electrode geometry can be

### 3.3 Conductivities

#### Solutions with low dissolved salt concentrations

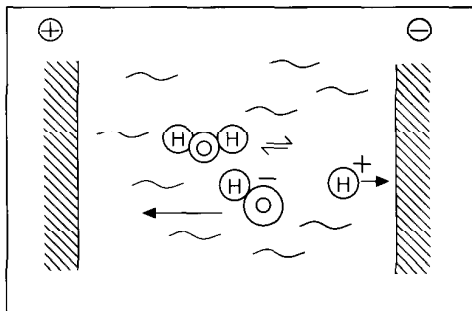
The conductivity of a solution is to a first approximation linearly dependent on the concentration of dissolved ions. As the concentration drops toward zero – e.g. as is the case in a good deionization plant, the conductivity drops only as far as a limiting value.

The reason for this is the property of water to self dissociate giving the ions: protons (H<sup>+</sup>) and hydroxyl ions (OH<sup>-</sup>). (This property is already explained in the discussion of pH.)



In a neutral and pure water the concentration of both ions is about 10<sup>-7</sup> mole/l – i.e.. a dissolved salt concentration of about 2 ppb.

*Dissociation of water contributes to total conductivity*

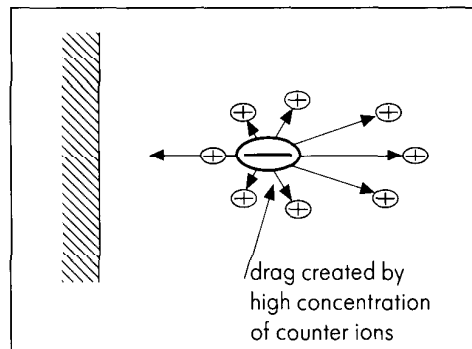


#### Solutions with high dissolved salt concentrations

In the medium concentration range (1 μmole/l – 1 mole/l), there is a reasonably linear dependence of the conductivity on concentration. As the concentration increases, however, the ions become more closely packed in the solvent and the electrostatic forces between them becomes more noticeable.

We have already seen, that such close packing screens protons and reduces the acidity of the solution through lowering the activity coefficient (Appendix). Conductivity is also affected. Increasing the concentration has less effect on the conductivity than expected because the ions tend to move as less mobile clusters rather than independently.

An additional effect is observed at yet higher concentrations. If the solute is a liquid e.g. sulfuric acid, at 100% solute concentration there is no water left. Since water has a very beneficial effect on the conductivity of ionic solutions – especially of acids or bases – this loss of solvent water leads to an absolute decrease of the conductivity.



*Drag at high concentration reduces the conductivity*

### 3.4 The measurement cell for conductivity

SIGNET conductivity cells are simple and robust constructions and are available with cell constants of 0.1, 1.0, 10.0 or 20.0 cm<sup>-1</sup>. The 0.1 cm<sup>-1</sup> cell gives the lower measuring resistance and is used for measuring low conductivity samples. For example, when this cell is used to measure pure water with a conductivity of 1 μS, the resistance given to the conductivity instrument is:

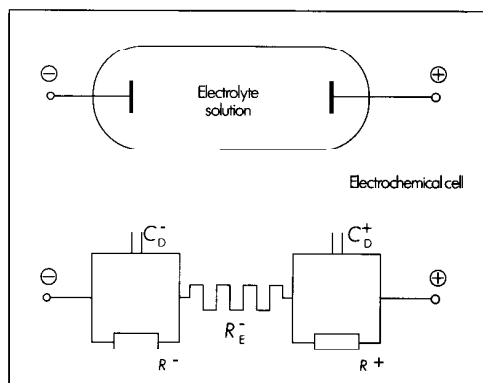
$$1 \text{ Mohm} \times 0.1 = 10 \text{ kohm}$$

The cell with constant 10.0 cm<sup>-1</sup> in comparison gives a 100 x higher resistance and would give an unacceptable high resistance in high purity water causing measurement problems. It is therefore used generally for medium to highly conducting samples.

A temperature sensor is incorporated in all sensors to allow automatic temperature compensation of the conductivity.

### 3.5 The electrical equivalent of the conductivity cell and the measuring principle

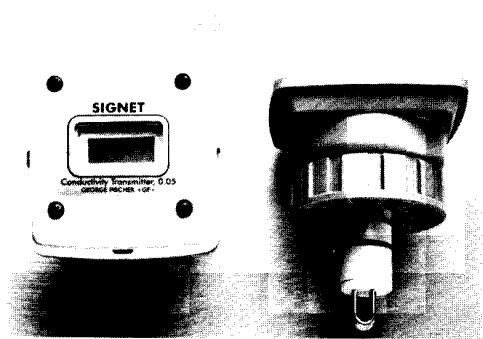
The standard conductivity measuring cell looks like a parallel plate condenser and it might be expected that as a result only an AC signal can pass through it. However, since the cell dips in a solution a conversion between electrical conduction and ionic conduction occurs at the electrodes through an "electrode reaction".



Electrical equivalent

The impressed electric current results in a chemical reaction at the electrode surface. The electrical equivalent of the simple conductivity cell therefore has to include a suitable electronic component to account for this electrode reaction.

SIGNET conductivity transmitter



The chemical reaction taking place is usually represented by a resistance component in parallel with the capacity term. Since this resistance is highly non-linear, the conductivity measurement is done by making sure that the energisation of the cell occurs through the capacity only. This is achieved by energising with an AC signal of low amplitude in the low kHz region. For accurate

measurements the conductivity of the sample must be negligible in comparison to that of the electrode interface. Thus a conductivity measurement with such an electrode configuration is not suitable for highly conducting solutions. Here the so-called inductive measurement principle must be employed.

### 3.6 SIGNET conductivity instrumentation

George Fischer offers a complete line of conductivity instruments and sensors ranging from a 2-wire, 4-20 mA conductivity transmitter model SIGNET 8800 to the SIGNET 9050 Inteltek-Pro Conductivity controller.

The SIGNET 9050 conductivity controllers are designed for exclusive use with the SIGNET 2820 series sensors, covering ranges from 1 to 200,000  $\mu\text{S}/\text{cm}$ , temperature compensated. Modular output cards enable many different interface configurations to meet the requirements of the user. All set-up, calibration and operation instructions are accessed and programmed from the front panel of the instrument.

Conductivity sensors are offered with a cell constant ranging from 0.1 to 20.0 including a temperature measuring element for temperature compensation.

### 3.7 Applications

#### Water Treatment

Water treatment plants utilizing deionization and membrane separation (reverse osmosis) represent the most widespread use of conductivity measurements. It is not surprising that the conductivity measurement is employed here since it measures exactly what the plant is doing – removing dissolved ions. The conductivity analyzer has to check that the equipment is working correctly – for example ion exchange resins become exhausted with time – indicated by so-called break-through of ions – at which time the conductivity increases sharply and the unit must be taken off-line and regenerated.

Reverse Osmosis plants also operate using conductivity as their primary control. A comparison of the feedwater conductivity to the product water conductivity can be calculated, and is termed "Percent Reject". This term literally quantifies the percent of salts in the stream that have been successfully rejected. Over time, the percent reject of the membranes will decrease, and at a predetermined level, the membranes can be taken off line, backwashed, etc. to help restore them to their optimum performance

### **Rinse baths**

Rinse baths are used in all metal-finishing operations. The task is to wash and remove chemicals from the article before proceeding to the next processing bath. The rinse water is often recycled or replenished with clean water to prevent the contamination (salts) from building up in the bath. Usually a conductivity measurement is employed, whereby a particular conductivity set-point based on experience is programmed to correspond with the maximum allowed contamination.

## **3.8 Not recommended applications**

In the power industry it is the modern practice to employ the so-called non-linear temperature compensation in the measurement of the conductivity (resistivity) of high purity water. Non-linear temperature compensation accounts for the fact that at high dissolved salt concentration the temperature coefficient is low (2-3 %/degree) whereas at low dissolved salt concentration the conductivity results mainly from dissociation of the water itself – a process having a high temperature coefficient (10%/degree). Since the sample temperatures are high, accurate temperature compensation is important. Moreover, since the samples are highly pure the conductivity lays in the difficult region of high temperature coefficient. Here, only an exact modelling of the temperature dependence through a "non-linear" method provides a satisfactory measurement.

*The possibility to set a high but fixed temperature coefficient cannot be considered to be a satisfactory solution for sophisticated high purity water applications (power utilities).*

# Appendix I

## pH - more theory!

### 1. The Nernst equation

The Nernst equation is an important one in the application of electrochemical techniques for analysis. It describes the variation of measured potential with pH or the composition of a solution of oxidizing/reducing species. The Nernst equation is derived from equilibrium thermodynamic considerations – i.e. purely on the basis of the energies of the species involved with no regard for kinetics i.e. how fast processes can occur. In other words the Nernst equation has been derived for and can only be applied to a system in energetic equilibrium with no net change from one species to another.

**In the case of the glass electrode the Nernst equation is:**

$$\begin{aligned} E &= E^0 + (RT/nF) \ln a_{H^+} \\ &= E^0 + ((RT/nF) \ln(10)) \log(a_{H^+}) \\ &= E^0 - ((RT/nF) \ln(10)) \text{pH} \end{aligned}$$

At 25 °C the value of  $(RT/nF \ln(10))$  is 59.16 mV. This is the slope factor. The offset factor is  $E^0$ . It is the sum of several terms, the most important of which are the standard potentials of the reference electrodes in the pH sensor.

**For a ORP system the Nernst equation becomes:**

$$E = E^0 + (RT/nF) \ln (a_{ox}/a_{red})$$

**Thus for the ORP reaction:**

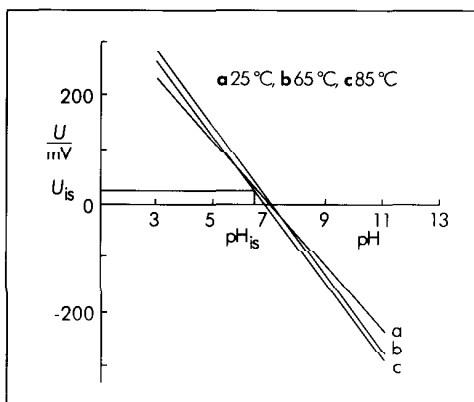


**Nernst becomes:**

$$E = E^0 + RT/nF \ln (a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}})$$

We see here a basic difference to the pH case – that at least two concentrations are involved. This makes a concentration determination more difficult. (In principle this is also the case for pH:  $E = E^0 + RT/nF \ln (a_{H^+}/a_{H_2})$ , however, since the reduced species is hydrogen gas which has by definition unit activity it disappears from the equation).

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*Isothermal point*

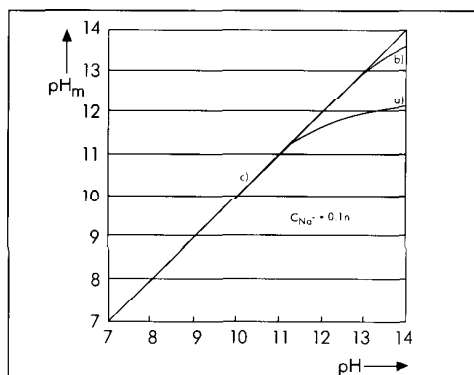
### 2. The temperature behavior of the glass electrode

We have seen that the pH electrode has been designed to give 0 mV signal at pH 7. However, what happens when the temperature changes. Since  $E^0$  also has a temperature coefficient, it would most likely result in the calibration curve shifting from the desired zero point at pH 7. Automatic temperature compensation would be inconvenient in such a case. For this reason the two reference electrodes have been designed as a pair to give a zero  $E^0$  temperature coefficient. This ensures that all calibration plots at different temperatures all cross the isopotential point i.e. at pH 7 and 0 mV.

### 3. The alkali error

No specific ion sensors are completely specific to the designated ion. There is always some interference. In the case of the glass electrode the interference is noticed:

- when the concentration of protons is low – i.e. in alkaline solutions
- when the concentration of the interfering ion is high.



*The sodium/alkali error*

The ion causing the greatest problem is sodium. Thus the worst case conditions are the measurement of sodium hydroxide solutions. Typical pH electrodes give zero error at pH values below 12.3 and rise to an error of 0.7 pH at pH 13.5.

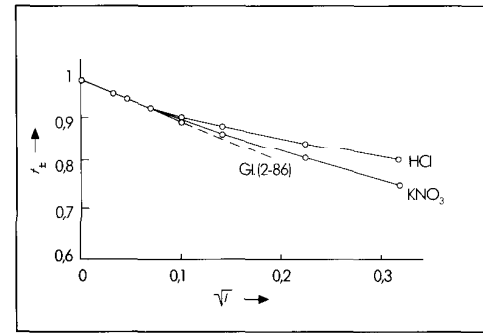
To account for cross-sensitivities the Nernst equation must be extended as follows:

$$E = E^0 + RT/nF \ln ( a_{H^+} + K a_{Na^+} )$$

where the term  $K a_{Na^+}$  corresponds to the response of the glass electrode to sodium and will have increasing importance at low proton activities and high sodium activities. Low sodium errors are given by electrodes having a low sodium cross-sensitivity factor  $K$ .

#### 4. The effect of the concentration of dissolved salts on the measured pH

The pH is a measure of the acidic activity of a solution. If the solution has a low concentration of dissolved salts then the activity is the same as the concentration. As the concentration of dissolved salts increases, then there is ever increasing interaction between the ions of the salts. Thus negatively charged ions become shielded by a shell of positively charged ions and vice versa. This effectively reduces the acidic activity, thus there is a deviation from the equivalence of activity and concentration:



Variation of activity coefficient with concentration

# Appendix II

## Applications

### II.1 pH measurements in drinking water plants

There are many opportunities for installing pH instrumentation in potable water treatment. This is because the dissolved salts in potable water can cause scaling and disposition if the pH is too high. If the pH is too low corrosion of the distribution pipelines may be accelerated. Several processes can result in pH changes - hence the need for pH control.

The pH should be monitored in the following stages of the water treatment:

- raw water feed
- coagulant addition
- manganese removal stage
- precipitation softening
- recarbonation
- de-alkalization
- de-alkalizer waste control
- aeration

Note: Not all of the mentioned processing stages will necessarily be employed in a particular plant.

#### Raw water feed

Monitoring the raw water feed is required for the intake protection. This is especially necessary with river water which can undergo changes in 30 minutes. Ground waters on the other hand are more predictable and show only seasonal changes.

The electrode chosen for monitoring raw water should withstand suspended mineral particles, decaying vegetation and bacterial slime etc. The low conductivity ( $\ll 150 \mu\text{S}/\text{cm}$ ) can cause measuring problems.

#### Coagulant addition

Coagulation treatments employ iron, aluminium or cationic polymer coagulants. The pH must be controlled for optimal treatment efficiency. The elec-

trode will be subject to fouling by the floc particles. Aluminium coagulants require a tight pH range of 5.5 to 7.5 to be effective.

#### Manganese removal stage

Magnesium removal requires use of oxidizing conditions generated by aeration or use of an oxidizing agent. Aeration requires a pH of 9-9.5, or when using a stronger oxidizing agent pH 6.5 may suffice.

Fouling of the pH sensor is likely to be a serious problem. Appropriate cleaning or anti-fouling techniques which can deal with soft deposits of hydrated manganese IV oxide are required.

#### Final water pH control

According to AWWA guidelines the final treated water must have a pH in the range 6.5 - 9.5. A reliable and stable sensor should be employed. Frequent calibration may be necessary to achieve the desired resolution.

#### Precipitation softening

Precipitation softening is carried out in sedimentation basins or pellet reactors. Control of the lime dose is achieved by monitoring the pH within the mixing tank prior to the sedimentation tanks or in the case of the pellet reactors at their outlet.

#### Recarbonation

Water softened by the precipitation method can be stabilized by re-carbonating with carbon dioxide. Control of the carbon dioxide dose rate is achieved by monitoring the pH of the recarbonated water.

#### De-alkalization

De-alkalizers employing a weak proton ion exchange resin can be controlled automatically by monitoring the pH of the softened water. A freshly regenerated exchanger will have an outlet pH around 3.4. As the exchanger becomes exhausted the pH rises. At pH 5.5 to 6.5 the exchanger must be regenerated with hydrochloric or sulfuric acid. To maintain a good exchanger performance it must be exhausted to the same

degree before regeneration. A reproducible pH measurement provides this capability.

### De-alkalizer waste control

The spent regeneration chemicals used for the ion-exchanger must be neutralised with caustic in a standard neutralisation tank. This is a straightforward pH control task.

### Aeration

Forced aeration may be employed to reduce the excess of carbon dioxide in solution following de-alkalization or to raise the oxidation potential for the removal of manganese. Monitoring or control of the aeration stage is required to avoid raising the pH of the water to a value at which the precipitation of calcium carbonate may occur.

Those processes where an oxidation is performed - manganese removal (aeration of water or use of oxidizing agents) can benefit from an on-line ORP sensor.

neutral and deficient in any harmful micro-organism.

The pH of the exposed water changes with time because of the equilibrium between the dissolved carbonate/bicarbonate salt and the carbon dioxide in the air. The pH increases. This is bad because it can cause skin irritation.

Micro-organisms find the oxygen rich water of a swimming pool the ideal place to grow. These natural processes must be prevented and belong to the normal swimming pool "maintenance" just like continuous filtering of the water.

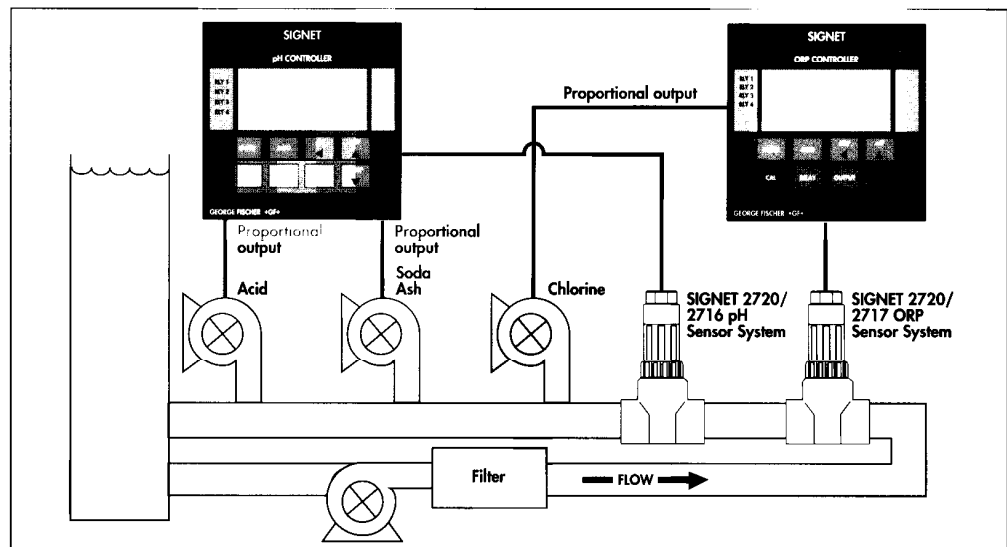
The most commonly used chemicals are hydrochloric acid (to maintain pH neutrality) and a powerful oxidising agent (previously chlorine or hypochlorite but more popular now ozone and chlorine dioxide) to destroy micro-organisms. pH control is the right choice for the dispensing of the hydrochloric acid - since the desired parameter is pH with a neutral value (pH between 7.4 and 7.6).

## II.2 Swimming pool chemistry control

Ground water contains many dissolved salts. A relatively high proportion is carbonate or bicarbonate. In addition living material (bacteria, micro-organisms) is also present. The ideal water conditions in a swimming pool are pH

In the case of oxidizing agent addition, the addition can be controlled with an ORP measurement. In 1982, the "Deutsche Institut für Normung (DIN)", adopted an ORP standard of 750 mV for public and commercial swimming pools. France and most other European countries have since adopted this standard.

A typical pH and ORP control of a commercial or public swimming pool



# Appendix III Useful tables

## III.1 pH of some Clark and Lubbs Buffer Solutions at 25°C

pH	Solution
1.0	25 ml 0.2M KCL + 67.0 ml 0.2M HCL diluted to 100 ml
2.0	25 ml 0.2M KCL + 6.5 ml 0.2M HCL diluted to 100 ml
3.0	50 ml 0.1M KH Phthalate + 22.3 ml 0.1M HCL diluted to 100 ml
4.0	50 ml 0.1M KH Phthalate + 0.1 ml 0.1M HCL diluted to 100 ml
5.0	50 ml 0.1M KH Phthalate + 22.6 ml 0.1M NaOH diluted to 100 ml
6.0	50 ml 0.1M KH <sub>2</sub> PO <sub>4</sub> + 5.6 ml 0.1M HCL diluted to 100 ml
7.0	50 ml 0.1M KH <sub>2</sub> PO <sub>4</sub> + 29.1 ml 0.1M HCL diluted to 100 ml
8.0	50 ml 0.1M KH <sub>2</sub> PO <sub>4</sub> + 46.7 ml 0.1M HCL diluted to 100 ml
9.0	50 ml 0.1M KCl/H <sub>3</sub> BO <sub>3</sub> + 20.8 ml 0.1M HCL diluted to 100 ml
10.0	50 ml 0.1M KCl/H <sub>3</sub> BO <sub>3</sub> + 43.7 ml 0.1M HCL diluted to 100 ml

## III.2 The pH of some common products

pH	Product
14	Lye
13	0.1M NaOH solution
12	Photodeveloper
11	Ammonia
8.2	Baking Soda
7.35	Human Blood
7.0	Pure Water
6.0	Milk
5.0	Coffee
4.0	Yogurt
4.5	Beer
3.5	Wine
3.0	Vinegar
2.8	Cola beverages
2.0	Lemon Juice
1.0	Gastric Juice
0.0	1M HCl solution

## III.3 Some ORP potentials

Reaction	E <sup>0</sup> (V)
Li → Li <sup>+</sup> + e <sup>-</sup>	-3.045
K → K <sup>+</sup> + e <sup>-</sup>	-2.925
Na → Na <sup>+</sup> + e <sup>-</sup>	-2.713
Mn → Mn <sup>2+</sup> + 2e <sup>-</sup>	-1.168
Ti → Ti <sup>2+</sup> + 2e <sup>-</sup>	-1.63
OH <sup>-</sup> → OH + e <sup>-</sup>	-1.2
Cr → Cr <sup>2+</sup> + 2e <sup>-</sup>	-0.913
Fe → Fe <sup>2+</sup> + 2e <sup>-</sup>	-0.440
Cr <sup>2+</sup> → Cr <sup>3+</sup> + e <sup>-</sup>	-0.107
4OH <sup>-</sup> → O <sub>2</sub> + 2H <sub>2</sub> O + 4e <sup>-</sup>	-0.401
2I <sup>-</sup> → I <sub>2</sub> + 2e <sup>-</sup>	-0.400
Ti <sup>2+</sup> → Ti <sup>3+</sup> + e <sup>-</sup>	-0.37
Ni → Ni <sup>2+</sup> + 2e <sup>-</sup>	-0.250
Pb → Pb <sup>2+</sup> + 2e <sup>-</sup>	-0.126
Fe → Fe <sup>3+</sup> + 3e <sup>-</sup>	-0.037
H <sub>2</sub> → 2H <sup>+</sup> + 2e <sup>-</sup>	0.000
Fe <sup>2+</sup> → Fe <sup>3+</sup> + e <sup>-</sup>	+0.771
Ag → Ag <sup>+</sup> + e <sup>-</sup>	+0.799
Pb → Pb <sup>4+</sup> + 4e <sup>-</sup>	+0.80
3Br <sup>-</sup> → Br <sub>3</sub> <sup>-</sup> + e <sup>-</sup>	+1.06
2Br <sup>-</sup> → Br <sub>2</sub> + 2e <sup>-</sup>	+1.066
ClO <sub>2</sub> <sup>-</sup> → ClO <sub>2</sub> + e <sup>-</sup>	+1.16
Pt → Pt <sup>2+</sup> + 2e <sup>-</sup>	+1.188
Ag → Ag <sup>2+</sup> + 2e <sup>-</sup>	+1.369
2Cl <sup>-</sup> → Cl <sub>2</sub> + 2e <sup>-</sup>	+1.538
Pb <sup>2+</sup> → Pb <sup>4+</sup> + 2e <sup>-</sup>	+1.694
Ag <sup>+</sup> → Ag <sup>2+</sup> + e <sup>-</sup>	+1.939
2F <sup>-</sup> → F <sub>2</sub> + 2e <sup>-</sup>	+2.866

## III.4 The Conductivity of some common products

