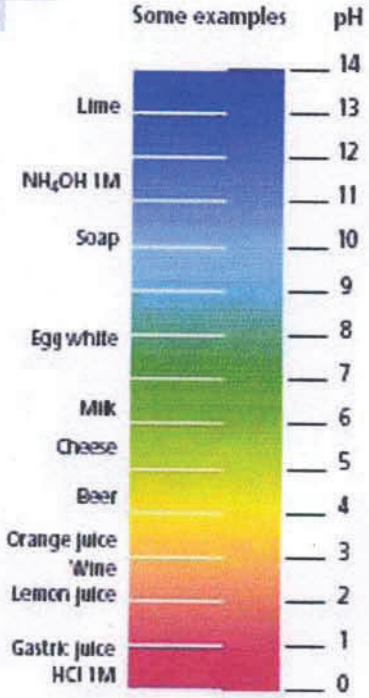
pH measuring. A little theory

pH

Determining the acidity of foodstuffs is probably the oldest type of analysis known to man. Taste was the first method he used.



The next step - slightly more scientific was the use of natural indicators, which would change colour depending on the acidity or alkalinity of an medium.
These indicators were the basis for the later invention of litmus paper.
These days, with the help of electrodes and pH-meters, it is easy to obtain a perfect quantification of acidity or alkalinity.

The term pH

It was Sörensen in 1909 who first introduced this term, describing it as the measurement of the acidity or alkalinity of an aqueous solution, defined as the negative logarithm of the concentration of H^+ ions.

$pH = - \log [H^+]$

The number of protons (H^+) that a substance contains gives the degree of acidity or alkalinity.
In other words, a high concentration of protons means that the substance has a highly acid pH, and a very low concentration of protons means that the substance has an alkaline pH.

pH range

Zone	pH	[H+] (mol/l)	[OH-] (mol/l)
	0	1	0.00000000000001
	1	0.1	0.0000000000001
	2	0.01	0.000000000001
acid	3	0.001	0.00000000001
	4	0.0001	0.0000000001
	5	0.00001	0.000000001
	6	0.000001	0.00000001
neutral	7	0.0000001	0.0000001
	8	0.00000001	0.000001
	9	0.000000001	0.00001
	10	0.0000000001	0.0001
alkaline	11	0.00000000001	0.001
	12	0.000000000001	0.01
	13	0.0000000000001	0.1
	14	0.00000000000001	1

These days the measurement of pH is absolutely necessary in all kinds of industry, not only in the analysis of foodstuffs.

Why do we measure the pH?

Correct measurement of pH ensures that we can:
- manufacture high-quality products
- obtain products with defined and constant characteristics.
- reduce production costs.
- ensure that we are not damaging the environment or harming people.
- comply with legal standards.
- increase our level of knowledge about different materials.

How is the pH measured?

To measure pH we need a pH electrode and an instrument: a pH-meter. CRISON recommends the use of a temperature sensor when analysing samples at different temperatures. If a stirrer is also used the results can be obtained much faster and much more precisely.
These days, this type of analysis is so important that the results obtained need to be computer-processed, which is why the instruments need to be connected directly to a PC, to make it easier to capture and process the data.

pH sensor, glass electrode

This is an electrode that generates an electrical signal proportional to the pH, according to Nernst's law. A number of aspects of this signal are taken into account:

Zero point: pH value at which the electrode generates a potential of 0 mV. This value is around pH 7 in most electrodes.

Asymmetry Potential: mV's generated by an electrode when immersed in a solution of pH 7. This usually oscillates around ± 20 mV.

Slope: Electrode response expressed in mV per pH unit. The theoretical slope of an electrode at a temperature of 25 °C is 59.16 mV/pH. In new electrodes, the slope is close to the theoretical value.

Sensitivity: This is the expression of the electrode slope in relative terms. It is obtained by dividing the real value of the slope by the theoretical value and is expressed as a %.

Asymmetry potential and sensitivity vary with the age and use of the electrode. Regular calibration is therefore required.

Calibration with buffers

This process involves adjusting the values read by a pH measuring system (instrument and electrode set) according to the values of buffer solutions (standards).
This compensates the deviations of zero potential and slope of the electrode that occur over time.

Frequency of calibration

This depends on the accuracy required by the user and the effect of the samples on the electrode. CRISON recommends daily calibration, but users should decide on the appropriate frequency, based on their own experience.

Stirring and pH

The use of a magnetic or rod stirrer improves the quality of measurements by increasing the response speed and the reproducibility of the measurements.
The stirring speed should be moderate and be identical for both buffers and samples.

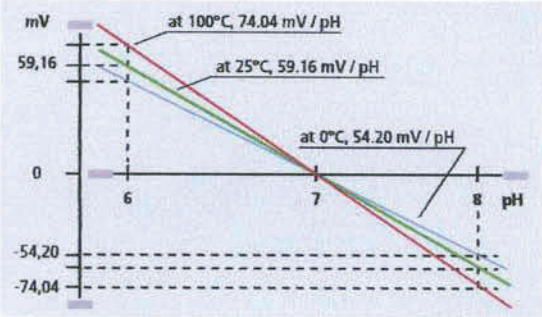
Automatic temperature compensation

To measure pH correctly, the results should always be expressed with the temperature at which the reading was taken.
Example: the pH 7 buffer solution gives 7.00 at 25 °C and 6.97 at 50 °C.

Effects of temperature in measuring pH ...

... on the electrode

Nernst's Law says that the electrode slope varies according to temperature in a predictable manner.



pH-meters automatically compensate for this effect with Automatic Temperature Compensation.
To do this, the temperature of the sample must be given to the instrument. This can be done by:

- Connecting a temperature sensor to the pH-meter, in addition to the electrode.
- Using an electrode with a built-in temperature sensor, the main advantage of this being that it makes handling easier. The two signals – pH and temperature – are transmitted to the instrument using a single sensor and a single cable.
- Manually entering the temperature.
  In some applications, temperature does not need to be measured, either because the temperature is constant or because a broad pH value is acceptable, etc. In these cases, the temperature of the sample can be entered manually using the keypad on the instrument.

... on buffer solution

Temperature makes each solution behave in a certain way.
CRISON pH-meters have a built-in table of the pH values of buffer solutions at various temperatures to obtain perfect calibration at any temperature.

... on a given sample

Temperature makes the pH of products vary in different ways, so the instrument cannot compensate for this variation. Therefore, the pH value and the temperature at which the measurement was taken must always be reported together.

Errors in pH measurement without compensation for the temperature, calibrating at 25°C

	pH										
°C	2	3	4	5	6	7	8	9	10	11	12
5	0.30	0.24	0.18	0.12	0.06	0	0.06	0.12	0.18	0.24	0.30
15	0.15	0.12	0.09	0.06	0.03	0	0.03	0.06	0.09	0.12	0.15
25	0	0	0	0	0	0	0	0	0	0	0
35	0.15	0.12	0.09	0.06	0.03	0	0.03	0.06	0.09	0.12	0.15
45	0.30	0.24	0.18	0.12	0.06	0	0.06	0.12	0.18	0.24	0.30
55	0.45	0.36	0.27	0.18	0.09	0	0.09	0.18	0.27	0.36	0.45
65	0.60	0.48	0.36	0.24	0.12	0	0.12	0.24	0.35	0.48	0.60
75	0.75	0.60	0.45	0.30	0.15	0	0.15	0.30	0.45	0.60	0.75
85	0.90	0.72	0.54	0.36	0.18	0	0.18	0.36	0.54	0.72	0.90

W/o error | Error < 0.1 pH | Error > 0.1 and < 0.3 pH | Error ≥ 0.3 pH

GLP (Good Laboratory Practice)

Good Laboratory Practice when measuring pH

The GLP guidelines have been drafted to guarantee the quality and validity of analyses in laboratories.
The requirements are as follows:

- The instrument must perform an autotest.
- The instrument must compensate automatically for the analogue drift.
- There should be a "password" to protect the measurement programmes.
- The value of the measurement should only appear when the point of stability is reached. It should be impossible to get an incorrect reading.
- Possibility of printing out reports, with the date and time of the measurement or calibration in the header.
- Easy access to the instrument's programs.
- Calibration data; asymmetry potential, slope, date and time.
- "Calibration expired" message.
- It should be impossible to calibrate by differences in temperature between buffers.
- Fixed and compulsory calibration protocol with 2 or 3 certified buffers which the instrument can recognise.
- Calibration and measurement under identical conditions.
- Time control for the duration of the measurement and stirring speed.
- It should be impossible to obtain a measurement if the calibration is wrong.

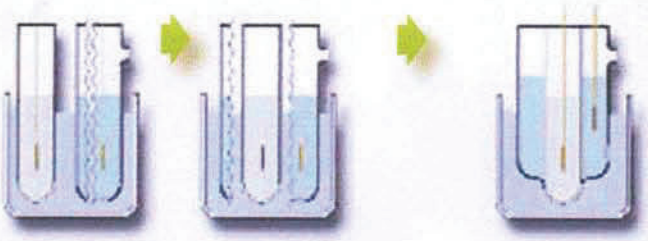
The GLP 21, 22 and PH-Burette 24 pH-meters have been specially designed to comply with DIN 19268 and with the precise specifications as given in the GLPs.

pH electrodes.
A little theory

Introduction
The pH measurement of a solution is based on transforming the electrical signal obtained by a glass electrode (indicator) and another reference electrode. According to Nernst's law, this signal is proportional to H^+ ion activity.
The potential of the glass electrode is directly dependent on the pH of the sample, whereas the reference electrode has a constant potential which is compared to that of the indicator electrode.

TWO ELECTRODES
GLASS + REFERENCE

Evolution
In 1948, Dr. Ingold made the first combined electrode. He merged the two electrodes, indicator and reference, into one.



EVOLUTION...

EVOLUTION...

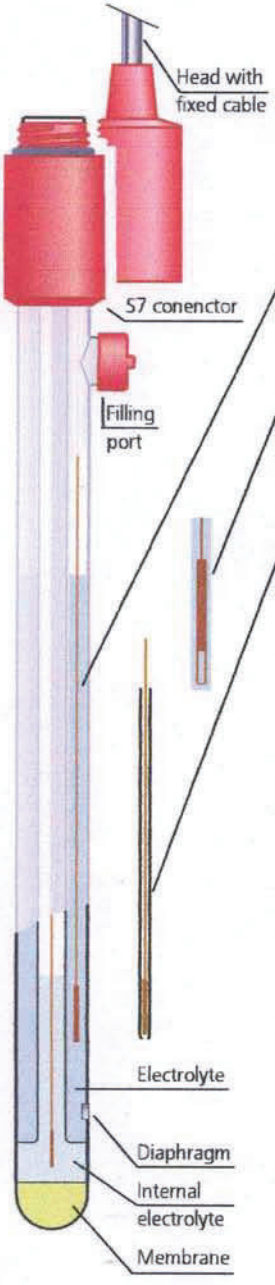
A COMBINED
ELECTRODE

Ever since they were invented, pH electrodes have evolved to adapt to the most diverse measuring conditions.

Electrodes with temperature sensors
Recent years have witnessed the appearance of combined electrodes with a built-in temperature sensor.
This allows us to measure pH and temperature simultaneously at the same point. This can be particularly important when calibrating with buffers.
The downside of these electrodes is that they are more expensive to replace.

The combined pH electrode. Essential components

Connector
Most lab pH electrodes have a S7 screw cap connector. In other cases, the cable is integrated with the electrode. These are called "fixed cable" electrodes.



Body material
Normally made of glass. In some cases, however, where required by the application, the body is made of plastic. This makes them stronger.

Reference element
This is a cell that supplies table potential (mV).
There are a number of types:

Silver wire (Ag)
This is galvanically-coated with AgCl and is the typical reference element for low-cost electrodes.

Encapsulated AgCl crystals
The silver wire comes into contact with a portion of the AgCl crystals inside a small glass tube.

Sleeved silver wire
Consists of a silver wire protected by a tube. Thus the reference element is protected from possible alterations which may occur in the electrolyte.

Electrolyte
This is a highly-concentrated saline solution into which the reference element is submerged.
It comes in 3 forms: liquid, gel or solid (polymer), depending on the type of electrode.

Liquid electrolytes. Used by refillable electrodes. There are a number of types for different applications. They are all KCl-based.

Gel electrolytes. These are used in non-refillable or low maintenance electrodes. Most are glycerine gels.
Eectrodes with wide PTFE diaphragm include a polyacrylic gel, thanks to which there is little electrolyte diffusion through the diaphragm.

Solid electrolytes. These are also used in non-refillable electrodes. They are made of a conducting polymer.

Diaphragm
This is the point of union between the sample and the electrolyte. It is the critical part of the electrode as it has a direct influence on its life-span.
A wide range of diaphragms are available. They vary according to manufacturer, application, quality of electrode and price.
This catalogue features electrodes with sleeve, ceramic, large and open diaphragms.

The sleeve diaphragm consists of a hole in the body of the electrode, half-closed by a PTFE ring. Its main features include a high electrolyte flow and the fact that it never gets blocked. It cannot withstand temperatures of over 60 °C.

The ceramic diaphragm is a chemically-inert, porous ceramic plate. These are the traditional diaphragms. They allow a small electrolyte flow towards the sample.

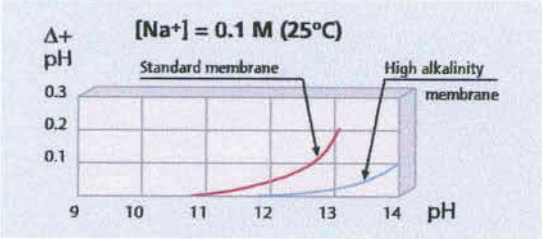
A large diaphragm consists of a large, porous PTFE ring through which contact between the electrolyte and the sample is made. One of the applications for this is the measurement of the pH of distilled water. It guarantees a large contact surface, with hardly any alteration of the level of conductivity of the sample. This is to do with the reduced flow of electrolyte provided by these electrodes, thanks to their polyacrylic electrolyte.

The open diaphragm, which should really be called without diaphragm , is actually a hole in the body of the electrode which allows the electrolyte to come into direct contact with the sample. It is only used with electrodes with solid electrolyte (polymerised). There is no electrolyte flow.

Glass membrane
The composition of the glass membrane affects characteristics such as sensitivity, chemical, thermal and mechanical resistance of the electrode or the scale of measurement, e.g. a pH of 0...12, of 0...14. There are membranes with specific types of glass, e.g.to measure pH in the presence of a certain concentration of HF.
There are also special membranes for measuring at very low temperatures (-30 °C).
The form of the membrane also varies, from classical cylindrical or spherical shapes to specific forms such as flat, pointed or micro.
A large membrane is a symbol of quality.
The speed with which an electrode responds depends directly on the quality of its membrane.

Alkaline error

Interference of the Na^+ ion, which manifests at pH > 12 and increases with temperature.
Under these conditions the pH measured is lower than the real pH. Specific membranes for high alkaline levels minimise this error.



Electrodes with pH scales 0...12 can occasionally measure higher values without undergoing changes, bearing in mind that the measurement will present a certain error *(see graph)*.

Practical considerations

Immersion depth

To obtain a correct measurement of the pH, the electrode must be immersed until the diaphragm is covered.

Flat membrane electrode, for superficial measurements. A drop of distilled water facilitates contact between the electrode and the sample.

Minimum volume of sample

This will depend on the shape of the recipient and the electrode used for the measurement.

Price-quality ratio

In practice, the quality of the electrode used has a direct bearing on the reliability of a measurement. CRISON only supplies top quality electrodes because experience has proven them to be a better investment in the medium and long-term.

Life of an electrode

The average life expectancy of a pH electrode is approximately one year, depending on use and maintenance given to it.
If your electrode has too short a lifespan, ask us about it; you could be using the wrong electrode!
Electrodes exposed to high temperatures do not last as long.
Very alkaline mediums also reduce the lifespan of electrodes.

Common problems

The use of the wrong electrode can cause a series of problems which can drastically reduce its lifespan. The most common problems, along with their causes and consequences, are:

- Diaphragm clogging.
  Open measurement circuit. Unstable readings...
- Reference system contamination.
  Shifting of pH values.
- Build-up of dirt on the membrane.
  Slow response and wrong measurements.
- Loss of sensitivity.
  Due to ageing or erosion of the surface of the membrane.
  Short-circuit in the connector.
- Lack of linearity.
  Membrane ageing or wear.
- Slow response.
  As per descriptions above.

Guarantee

CRISON electrodes are guaranteed for a six-month period.
The guarantee only covers manufacturing defects.
The guarantee does not cover defects that could arise from incorrect use, handling, application or maintenance, or as a result of premature wear inherent to certain samples.