the importance of
pH in water purification

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What is pH?

The pH scale has been in use for over a century, ever since it was first defined in 1909 by the Danish chemist, Søren Sørensen.

In simple terms, the pH scale provides a standardised method of measuring the acidity or alkalinity (basicity) of a solution. This is determined by the concentration of hydrogen ions that are present; the higher the concentration of hydrogen ions the greater the levels of acidity. The term pH is generally taken to be the abbreviated form of 'the power (p) of the concentration of the Hydrogen ion (H)'.

It should be noted that the scale is logarithmic and is calculated using the negative logarithm of the concentration of hydrogen ions, so that a lower pH represents a higher concentration of Hydrogen ions. The formula is: $pH = -\log [H^+]$ and is shown on a scale of 0-14. A solution with a pH less than 7 is an acid, 7 is neutral, while a solution with a pH higher than 7 is an alkali.

Because the scale is logarithmic, a pH of 3 is ten times more acidic than a pH of 4. Likewise, a pH of 3 is one hundred times more acidic than a pH of 5, while a solution with a pH of 11 is ten times more basic or alkaline than one with a pH of 10.

To put this into context, at a temperature of 25°C pure water has a pH of 7, lemon juice 2.4 and household bleach 12.5. As Sørensen was head of the Carlsberg Laboratory's Chemical Department when he introduced his scale of measurement, it's appropriate to note that the pH of beer is normally around 4.5.

Some years after his initial definition, in 1924, Sørensen realised that the pH of a solution was actually determined by the activity of the Hydrogen ions, not their concentration, and that activity levels are affected by changes in temperature.

A better definition of pH is therefore $pH = -\log[aH^+]$, where aH^+ denotes the thermodynamic activity of the ions. This has subsequently become the basis on which pH measurements, generally taken by special handheld or in-line meters, are now calculated and specified by various industry standards bodies.
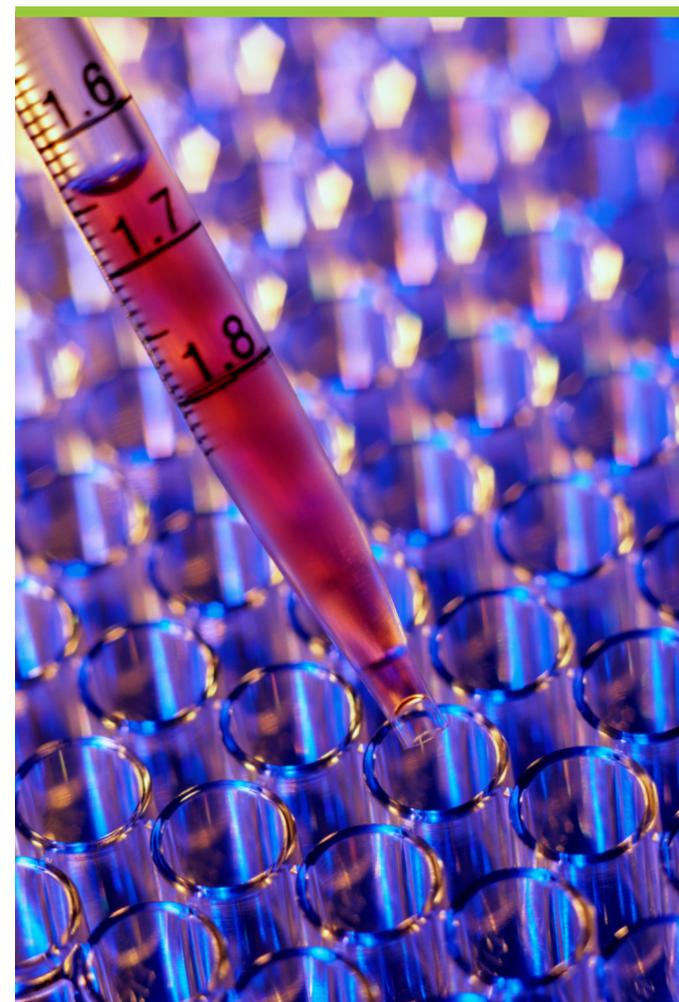
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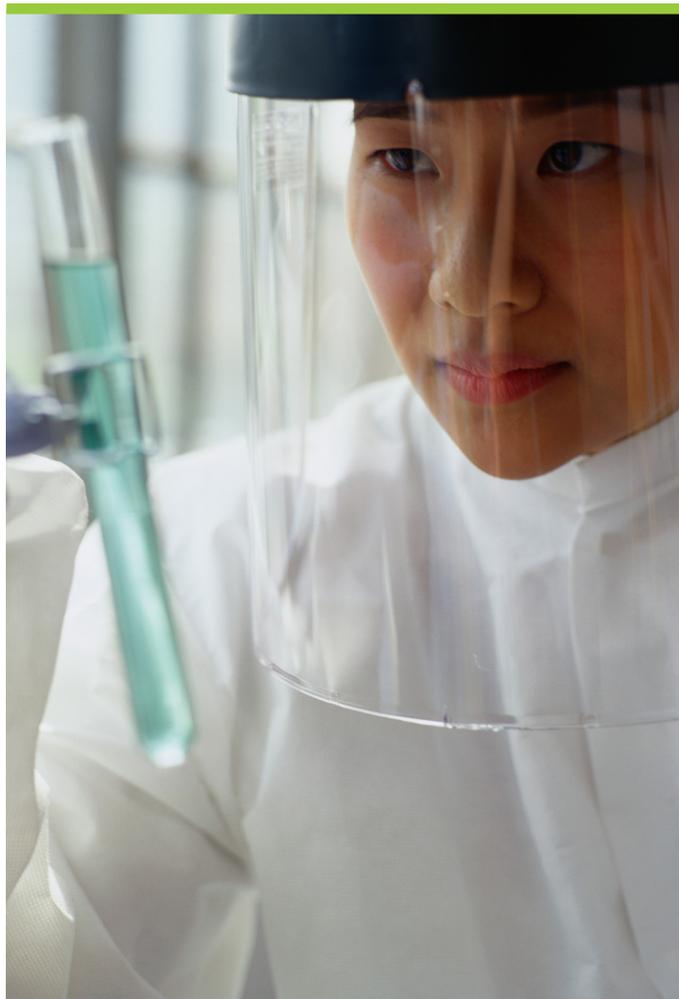
pH and conductivity

Measuring the pH of water used in laboratory, healthcare or industrial applications can be one of the quickest methods of determining its purity.

For example, dissolved gaseous contaminants such as air or carbon dioxide, as well as the presence of ionic salts, will affect pH readings, moving them further away from the neutral balance at a pH of 7.

Measuring pH accurately, however, can be a challenging process and prone to a number of induced errors, from both the sampling instruments and procedures.

An alternative is to capitalise on the ability of dissolved ions in a sample to conduct electricity. Using a conductivity meter it is possible to measure the flow of electricity through a fluid, with readings being directly proportional to the concentration of ions, their charge and levels of activity, or mobility.

The higher the readings – or the higher the conductivity – the greater the concentration of ions. The level of dissolved ionic material or salts is also referred to as total dissolved solids (TDS).

Ions can be positively charged cations (such as H^+, Na^+ and Mg^{++}) or negatively charged anions (such as OH^-, Cl^- and SO_4^{2-}). Although different ions move in solution at different velocities the most mobile of the common ions are Hydrogen $[H^+]$ and Hydroxyl $[OH^-]$; as a result, highly acidic or alkaline solutions will normally produce the highest conductivity readings.

Conductivity and its reciprocal, resistivity, can both be used to indirectly assess pH. Conductivity is measured in Microsiemens per centimetre (μS/cm) and resistivity in Meg Ohms centimetre (MΩ.cm). Ultra pure or deionised water, with a natural pH of 6.998, has a conductivity value of 0.055 μS/cm, or 18.2 MΩ.cm at 25°C. In practice, conductivity is generally used to measure water with a high concentration of ions and resistivity to measure water with low levels of ions.

It should be noted that changes in temperature can significantly affect the conductivity of a sample. In a typical mains water sample conductivity readings can change by around 2% per degree Centigrade, with the neutral pH of 7 only being accurate at 25°C; at freezing point, the neutral value is 7.5 and at 100°C the pH value is 6.2. As a result, conductivity measurements are internationally referenced to 25°C to allow for comparisons of different samples.

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pH vs Temperature (°C) graph showing two dashed curves: 0.5 ppm NH3 and Pure Water
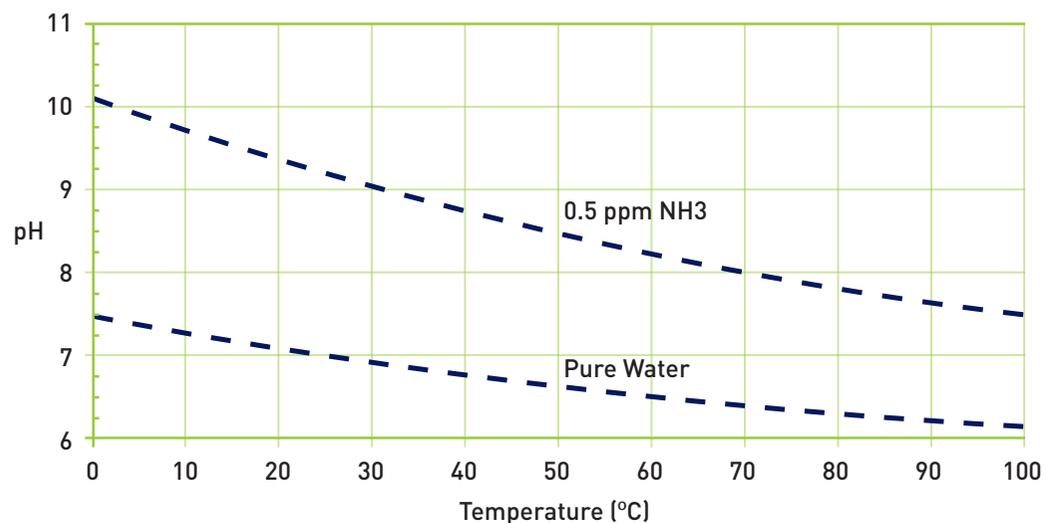
Measurements are normally carried out using handheld conductivity or resistivity meters, where probes are placed into the liquid sample. Older designs of instrument use two separate probes, while more recent meters have a single combined sensor.

In each case, the method of operation is similar, using a sensor that measures the concentration of Hydrogen ions against a reference source, with a separate temperature reading also being taken to allow the meter accurately to calculate the pH value. Many modern meters offer the ability to display a range of values, including resistivity, conductivity, TDS, as well as pH.

For more demanding applications in-line systems are generally used. These provide continuous monitoring to higher levels of accuracy, and are normally connected directly to automated higher level process control systems.

What can go wrong?

Relying solely on pH to measure water purity is an unreliable method for a number of reasons. Perhaps the most significant factor is that as soon as a sample of purified water is drawn from the system to be tested, and is exposed to the air, it will absorb carbon dioxide.

This reacts with the water to form carbonic acid in solution, which disassociates to release conductive ions. The result of a few parts per million (ppm) of CO_2 being dissolved in a sample of ultra pure water can be significant, reducing the pH level to around 4.0, even though the resistivity of the water – and its purity – is still at 18.2 MΩ.cm.

A pure water sample cannot therefore be held in a container with air, or exposed to air, without affecting the accuracy of measurement. The rate of contamination and effect on conductivity and pH levels will generally be rapid and is effectively a function of the surface area exposed and the time elapsed. For the same reason, samples should not be stored before pH levels are measured, while the sample containers used should be clean and manufactured from materials that will not leach contaminants into the sample. Similarly, sampling and measurement procedures should always be consistent to eliminate the risk of errors.

Sample contamination is one of the most common – and overlooked – causes for the incorrect interpretation of pH measurements. This can often lead to an erroneous assumption that as pH readings have changed between samples that a malfunction has occurred with water purification or process equipment.

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Ideally, pH measurements should be made on closed, flowing samples using in-line instruments. For laboratory sampling, best practice is generally to take a portable instrument to the source and ensure that the probe is fully immersed at the bottom of the sample container, with the sample being allowed to overflow.

A further problem is that the performance of pH probes or electrodes can also be influenced by the contaminants or ions in the water and by temperature.

These factors can be especially problematic in process or in-line applications, where fouling, scaling or chemical poisoning can rapidly affect the accuracy of readings and require instruments to be recalibrated at frequent intervals.

pH meters should also be used only for the applications for which they have been developed; in particular, they are generally calibrated for samples containing relatively high levels of contamination, which makes them unsuitable for use for accurately measuring the quality of ultra pure water unless they are fitted with specialised probes.

It is also important to maintain consistent sampling and testing procedures. For example, something as

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simple as a build up of salts on probes, a fluctuation in sample temperatures, or a change in personnel or test laboratory, can quickly lead to inaccurate and inconsistent readings.

By comparison, using conductivity probes offer a far more reliable method of determining water quality.

These instruments are simple to use, far less prone to the environmental effects that influence pH devices, and automatically compensate for fluctuations in temperature.
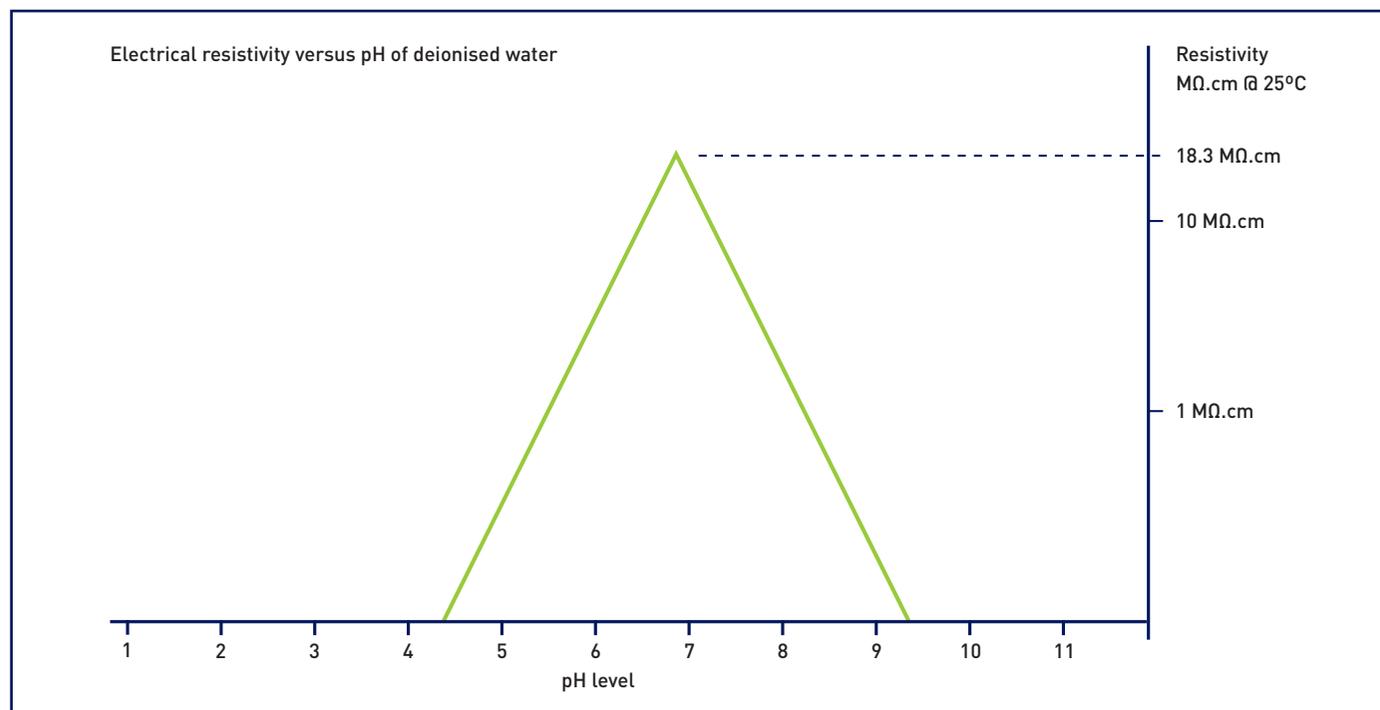
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Electrical resistivity versus pH of deionised water

Resistivity MΩ.cm @ 25ºC

- 18.3 MΩ.cm
- 10 MΩ.cm
- 1 MΩ.cm

pH level: 1 2 3 4 5 6 7 8 9 10 11