An introduction to the theory and practical methods for measuring pH

Table of Contents

1. COMMON TERMS for pH

1.1 What causes pH?

In its simplest form, pH is a measurement of the concentration of hydrogen ions (H+) or hydroxyl ions (OH-) in a solution. If both types of ions exist in a solution they will cancel each other out and the solution will be neutralised;

$$H^{+} + OH^{-} = H2O$$

This shows that the H+ and OH- will react together to give H2O, water.
The concentration of the hydrogen ions (shown as [H+]) is used to calculate pH using the equation;

$$pH = -\log10\ [H+]$$

The equation uses a logarithm base 10 this means that on the pH scale each whole number is ten times that of the one before it, e.g. a solution of pH 3 is ten times as acidic as a solution of pH 4

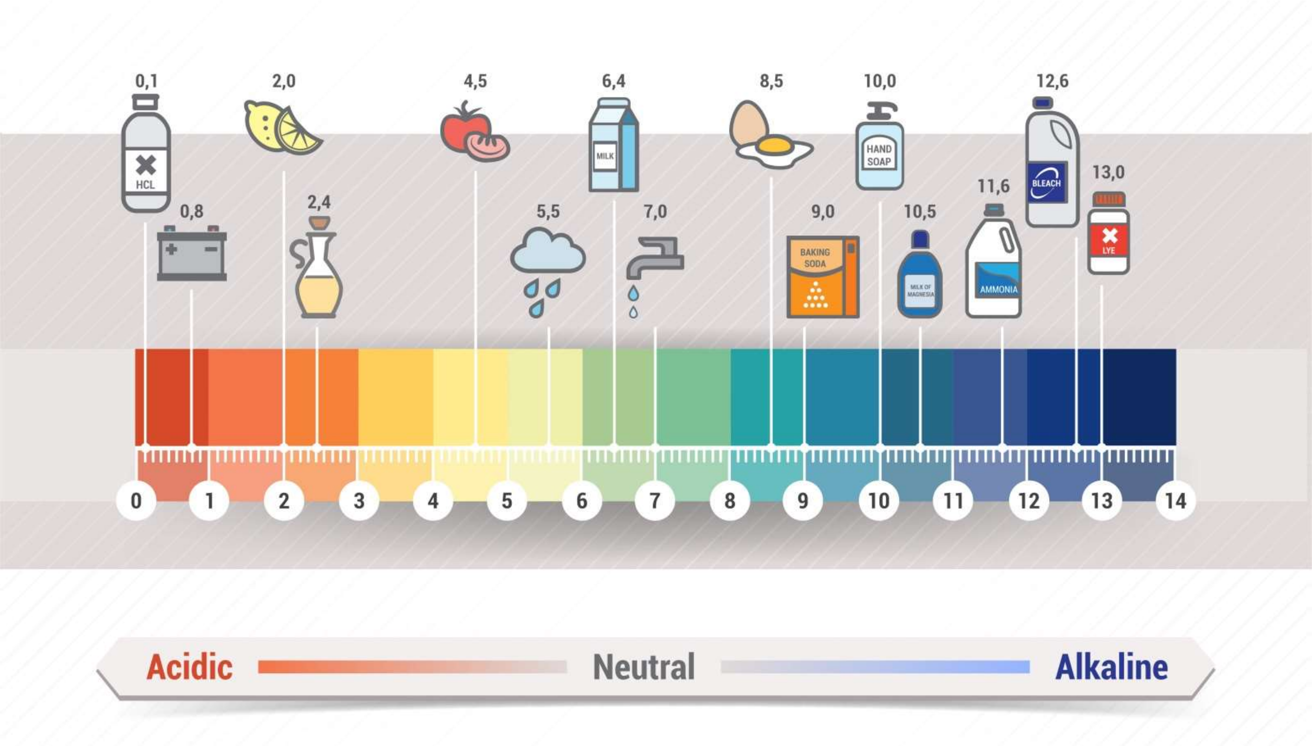
1.2 What do acid, alkaline and basic mean?

We can refer to solutions as acid or acidic meaning they have a high concentration of H+ ions.
Alkaline, alkali or basic solutions are those which have a high concentration of OH- ions.
These terms indicate that the solution will be at one end or the other of the pH scale, but do not tell us what the concentration of ions present is ñ two solutions may both be acid but might have very different concentrations of H+ ions.

Calculating the pH of a sample means that we have a number that defines how acid or alkaline the sample is, so we can compare it to others and see where it lies on the pH scale.

1.3 What is the pH scale?

The pH scale is the range of possible pH values that solutions can have.
This is the number given from the equation in question 1, but most methods of measuring pH will directly read out the pH value.
The scale runs from 0 to 14.



From 0 to 7 are acidic solutions, where H+ ions are present in greater concentration.
From 7 to 14 are alkaline solutions, where OH- ions are present in greater concentration.
At 7 in the centre of the scale are neutral solutions like water.

1.4 What different ways are there to measure pH?

pH can be measured by many different methods. You should choose which method to use based on the accuracy you need and the samples you are measuring.

pH test strips or test papers are a quick and simple way to give a rough measure of the pH. They are less accurate than other methods and are often used when an indication of the value is needed.
Methods such as test kits and comparators offer slightly more accurate measurement but are often limited to only being suitable for clear liquids.

pH meters are the most accurate way to measure pH, with resolutions of up to 0.001 pH available. They also offer the most versatility because they can be used with all sorts of samples even if they are solid or highly coloured ñ for example paints or food products. See more information about this in Section 2

1.5 What are pH buffers?

Buffers are chemical formulations which are designed to always have a set and accurate pH value.
These are used to calibrate pH measurement methods, especially electrodes for pH meters. Find out more about calibration in 1.6 below.

Buffers are available in a range of different formats (e.g. powders which must be made up into solutions on site, sachets of liquid for just one use, or bottles of bulk solution) but all will perform the same job.

1.6 What is calibration?

Calibration is the process of resetting an instrument against known standards to make sure that its readings are accurate.

For example, a pH electrode is calibrated using pH buffers. The buffers have a known and set pH value, e.g. pH 4 buffer will always have a value of pH 4. We can use this buffer to make sure the electrode is reading pH 4 correctly. Find out more about buffers in Section A Question 5
If the electrode reads pH 5 in a pH 4 buffer we know that this is incorrect and we can adjust the electrode to recognise that it is actually pH 4.

If we then also calibrate with another buffer at pH 7 this becomes a 2 point calibration. This means the electrode now has 2 reference points that it will refer back to when reading an unknown sample you want to measure.

Calibration effectively shows the electrode what pH 4 'looks like' so that later it can judge unknown samples against this.

2. INTRODUCTION TO pH METERS

2.1 Why use a pH meter?

pH meters are widely used to give accurate readings of pH in all sorts of settings from industrial sites to laboratories, environmental monitoring, food manufacturing, education and quality control.
pH meters are often chosen over other methods of measuring pH because they are faster, more accurate and more versatile.

Faster - results are faster than traditional methods such as titrations but also faster than many test kit methods.

More accurate - because the result is from an electronic sensor it is more accurate than methods like test strips and test kits that rely on judging a colour change by eye. There is also better resolution so results can be given down to 0.01 pH units even with most basic pH meters, while most pH strips or test kits will only offer resolution of full pH units.

More versatile - due to the wide range of specialised electrodes available pH meters can be used to measure almost any sample type - from water and chemical solutions right through to cheese, meat, fabric, fruit and vegetables, oils, paint, bread and dough, beer, and wine.

If you need to start testing a different sample type it is easy to buy just a new electrode and plug this into the meter you already have.

2.2 What are the different parts of a pH meter?

At a first look most pH meters appear to consist of just a few elements; the meter (which houses the electronics, the display screen and the control buttons), the electrode (which measures the samples) and some will have a separate temperature probe.

However there are more to each of these elements than it first appears. Understanding the workings of each element can help in troubleshooting and in choosing the right equipment for your sample type.

2.2.1 The Electrode

Although in most modern meters the electrode is just one piece, there are actually two component parts needed to read pH - the pH electrode and the reference electrode. Most modern electrodes have both components built into one for ease of use; hence these are sometimes referred to as '2 in 1 electrodes' or 'combination electrodes'. Find out more about this in Section 3

2.2.2 Temperature Probe

pH readings are affected by temperature, so most systems will include a temperature probe - also known as an 'ATC' or automatic temperature compensation probe.

The probe measures the temperature of the sample and adjusts the results accordingly. This means that temperature is no longer a variable, since it is corrected for in the results, so readings taken at different temperatures can be compared.

Find out more about the effect of temperature on pH in Section 5

3. pH ELECTRODES IN DETAIL

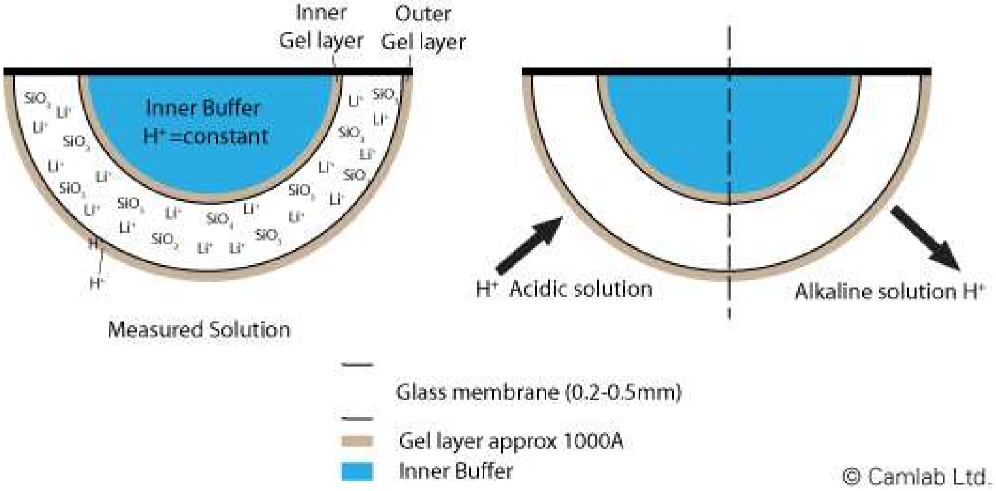
3.1. How does the electrode measure pH?

What we commonly refer to as a pH electrode is actually a 2-in-1 electrode which comprises of the pH electrode and a reference electrode built into one piece. Together these measure the pH of the sample.

3.1.1 pH electrode; The pH electrode consists of an internal buffer (electrolyte) which has a constant concentration of H+ ions. The glass containing this is sensitive to the H+ ions and forms a gel layer when in solution which the ions can move through.

Surrounding this is another outer glass layer, which again is sensitive to H+ ions and forms a gel layer in solution. This layer is exposed to the solution you are measuring.

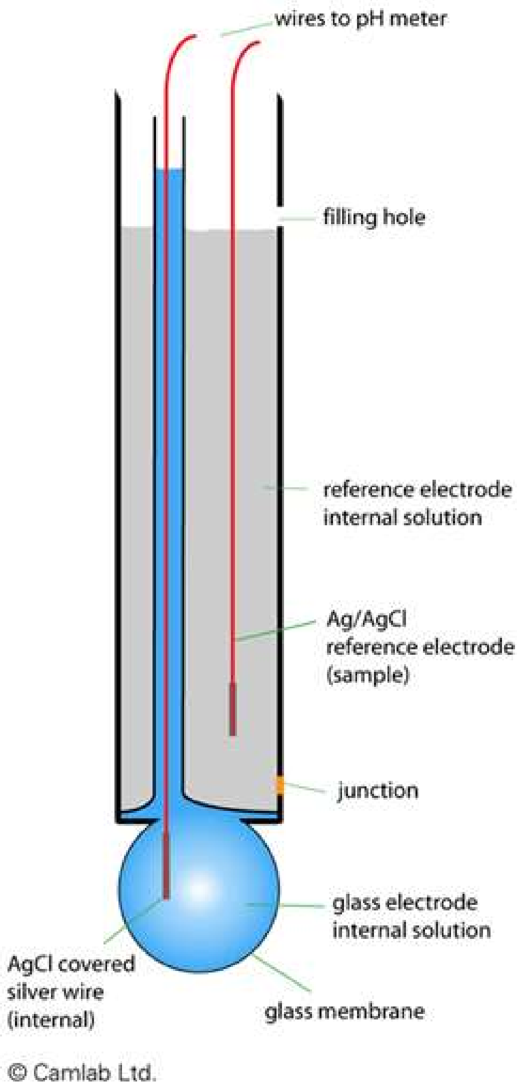
In acid solutions where the concentration of H+ ions in solution is high the H+ ions will move into the gel layer, giving a positive charge. In alkaline solutions where the concentration of H+ ions in solution is low, the H+ ions will move out of the gel layer and give a negative charge. This charge is compared to that of the internal buffer which has a constant concentration of H+ ions, and the difference or potential correlates to the pH.



Other Ions of similar size to H+ ions can interfere with this process (such as Na+ ions (sodium) or K+ ions (potassium). Measuring the pH of samples which contain high concentrations of these ions may take much longer as the H+ ions have to replace these other interfering ions in the gel layer before a stable potential is set up.

3.1.2 Reference Electrode; In order to give the pH reading the potential of the pH electrode has to be compared against a standard, this is where the reference electrode is used. The reference electrode is not sensitive to H+ ions. A junction in the reference electrode allows constant contact between the sample and the inner reference solution (often KCl Potassium Chloride solution) This gives a constant and stable potential which the potential of the pH electrode is compared to. The difference found from this comparison equates to the pH.

3.2 What are the different parts of an Electrode?



The diagram above shows the main parts of a traditional glass combination electrode. The main components which are changed from the illustration above to specialised electrodes are;

3.2.1 Junction – in traditional glass electrodes with a "standard" junction this is a porous ceramic material so that the internal reference electrode solution can very slowly flow out into the sample. If the sample contains certain species like proteins or sulphides the reference electrode solution can react with the sample and form a solid precipitate which blocks the pores of the junction material and stops the electrode from working. When KCl is the reference electrolyte the presence of Hg2+, Ag+, Pb2+ and ClO4- can form precipitates.

In specialised electrodes this junction is altered to prevent or reduce this clogging...

PTFE	These are often a larger surface area junction prevalent on flat surface designs. See Camlab Flat Surface Electrode
Double Junction	These designs incorporate a second chamber with a silver free electrolyte between the reference junction and a second sample junction to reduce contamination of the junction. See Camlab Double Junction electrodes
Liquid junction	This type of electrode creates a renewable liquid junction between a narrow opening of the reference part of the electrode. These electrodes offer superior performance and speed as the electrode can effectively be returned to 'new' condition at the press of a button. See Camlab Rapid Liquid Junction Electrodes
Open Junction	Where the reference electrode solution is replaced by a solid electrolyte.

3.2.2 Reference Electrode Internal Solution – for standard electrodes this is usually KCl (Potassium Chloride) saturated with AgCL (Silver Chloride). As this flows out of the electrode during its lifetime it must be refilled at intervals. In some electrodes this reference electrode solution has been replaced by a solid material which performs the same job. These are often referred to as “gel” type electrodes and do not need refilling.

3.2.3 Membrane Glass – this membrane must be in contact with the sample for the pH electrode part of the electrode to take a reading. In traditional electrodes this is spherical in shape as pictured above, but this is altered in electrodes for specific sample types. Find out more about the specialised shapes available in Section C Question 3

4. CHOOSING THE RIGHT ELECTRODE

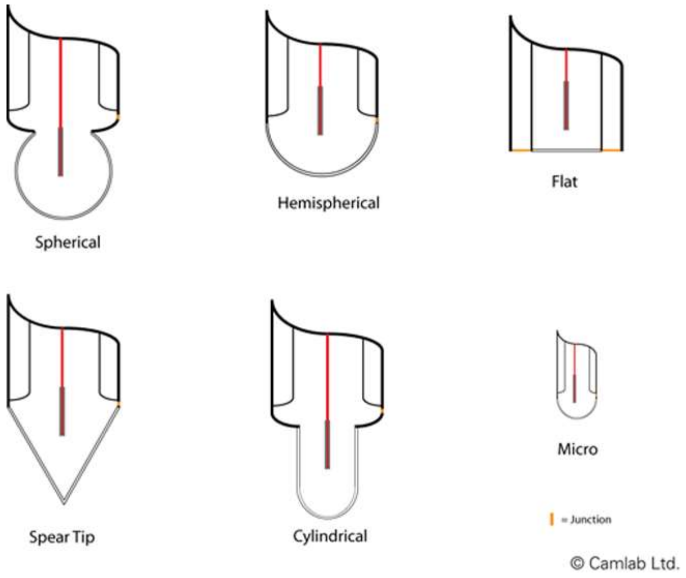
4.1 How should I choose an electrode?

The samples you are testing will be the main factor dictating the electrode you should use. Electrode selection tables and charts often give a good indication of the best electrode for the job - for examples see our table here. However these are just a guide and you may wish to consider some additional factors when choosing.

Things to consider might include;

Do the samples contain proteins, heavy metals or sulphides?	If yes you may need a specialised junction to prevent clogging. See Section C Question 2 and Question 4
Is a non-glass electrode needed - for example in food manufacturing?	Specialised ISFET probes do not contain any glass - see section C Question 5
Are the samples to be tested at very high or very low temperatures?	Check on the limits of the electrode as extreme temperatures can damage some types of glass
Do the samples contain HF - hydrofluoric acid?	A specialist electrode may be required to prevent the HF attacking the electrode glass
Are the samples very pure water or of low ionic strength?	A specialised electrode may be needed to obtain stable readings in reasonable time in low ionic strength samples
Are the samples solid or semi-solid, very low volume or in a small container, a flat surface or drops on a flat surface?	A specialised shaped electrode may perform best, see the image below;

A specialised shaped electrode may perform best. Typical examples are shown below



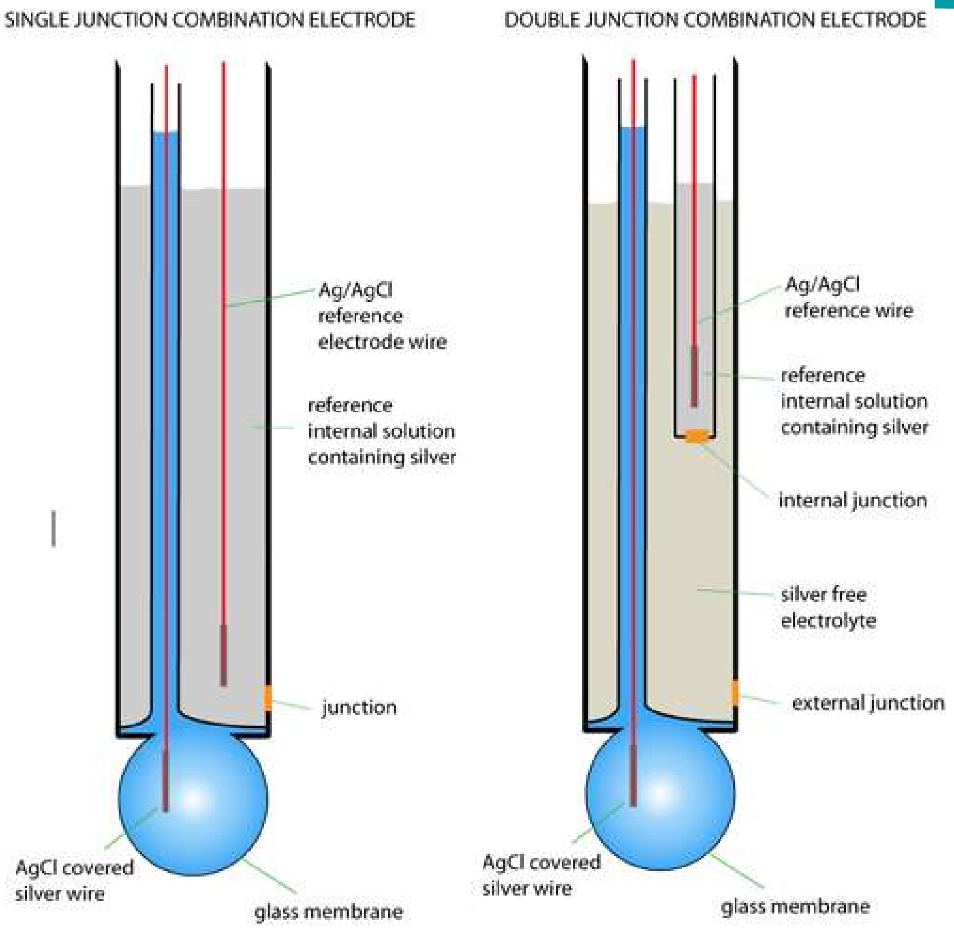
© Camlab Ltd.

Spherical - Ideal for low temperature as this shape bulb resists contraction but is easy to damage
Hemispherical - Good for small sample volumes and tends to be a bit stronger
Flat - For measuring surfaces, pastes etc. Small pH membrane area can be a bit slower but typically larger junction area is resistant to clogging.
Spear tip - For solids and semi solids allowing you to penetrate the sample material
Cylindrical - Highly sensitive membrane due to its large surface area giving lowers resistance
Micro - Very small design for narrow tubes

4.2 What does double junction mean?

We have already discussed that the reference electrode is in constant contact with the sample to create a constant potential (see Section C Question 1) and that this is achieved by a junction that allows some flow of the reference electrode electrolyte into the sample (see Section C Question 2).

In samples that contain certain species (including proteins or sulphides) the sample can react with the electrolyte and make a solid precipitate which blocks this junction (see Section C Question 2)
A double junction is one of the ways of preventing this reaction from occurring. The basic structures of a single junction and a double junction electrode are shown below.



© Camlab Ltd.

The double junction electrode features one junction from the reference electrode electrolyte to an intermediary silver free electrolyte, then a second junction from the intermediary to the sample. This means that the sample cannot come into contact with the silver ions in the reference electrode electrolyte which forms the junction blocking solid precipitates.

4.3 What does ISFET mean?

Some electrodes are referred to as ISFET ñ these are not based on the standard design but instead contain Ion Selective Field Effect Transistors. These work by the current through the transistor changing in response to changes in concentration of the ion ñ in the case of pH this will be H+ ions.

This type of electrode do not contain any glass so are often used in food manufacturing where glass presents a contamination risk to the products.

4.4 What is a 3 in 1 electrode?

Some electrodes contain the pH electrode, reference electrode and temperature probe in one piece; these are known as 3-in-1 electrodes. Find out more about the pH electrode and reference electrode in Section C Question 1. Find out more about the temperature electrode in Section C Question 8

4.5 What is an ATC probe?

pH readings are affected by temperature, so most systems will include a temperature probe ñ also known as an ATC or automatic temperature compensation probe.

This can be a separate probe which is put into the sample with the pH electrode, or it can be built in with the pH electrode.

The probe measures the temperature of the sample and adjusts the results accordingly. This means that temperature is no longer a variable, since it is corrected for in the results, so readings taken at different temperatures can be compared.

5. pH FACTORS

5.1 What factors might affect my pH results?

A variety of factors may affect the results of your pH measurements. Some key points are outlined below, but if you are still unsure your results are correct try consulting the troubleshooting guide. [to be added separately]

a. Temperature

The temperature of samples will affect pH due to a variety of reasons. Many of these factors can be corrected for with the use of temperature compensation (using a 3-in-1 electrode or an ATC probe, see Part C Question 7/8) but some cannot be corrected for by this.

To ensure accurate results the calibration and sample measurements should be conducted at the same or as close as possible temperatures.

b. Calibration intervals

Calibration must be performed at regular intervals to check that the electrode is still reading correctly. The principles behind calibration are explained in Section A Question 6. The exact frequency varies depending on the samples and conditions you are working in, the electrode type and the number of readings taken. It should be noted that calibration is electrode specific ñ this means if you use the same meter but use a new electrode, you should recalibrate.

c. Alkaline Error

This term is used to describe errors seen when Na+ (sodium) or Li+ (lithium) ions replace H+ ions in the gel layer on the electrode. See more about this in Section C Question 1.
This means in a sample that contains high concentrations of Na+ or Li+ ions the reading may appear lower than it should. This is usually only seen in high pH value (alkaline) solutions.

d. Junction blocking by incompatible species

Incompatible species in the sample can react with the liquid in the electrode and form a solid precipitate that blocks the junction of the electrode. See more detail in Part C Question 2.

e. Non-aqueous solvents

Measurements in organic solvents will not fall on the usual pH scale since the dissociation of the solvent molecules will be completely different to water. There are some methods to work around this and obtain relative measurements, but generally measurements in these solvents are not easy to do.

6. ELECTRODE MAINTENANCE

6.1 What Electrode maintenance is required?

Proper maintenance and cleaning of the meter and electrodes will ensure that they give accurate results and have a long life. The key items for everyday maintenance are;

Storage solution ñ this is usually 3.0M KCl solution and is sometimes mixed with a small amount of pH 4 buffer. pH electrodes should be stored in this when not in use to keep the glass membrane hydrated.

Cleaning solutions ñ electrodes should cleaned after use, especially if samples contain interfering molecules such as proteins or heavy metals. Specialised cleaning solutions to remove particular contaminants are available, or distilled water may be used to rinse off traces of samples or prevent carry over between different samples.

6.2 What is storage solution and why is it needed?

This is usually 3.0M KCl solution and is sometimes mixed with a small amount of pH 4 buffer. pH electrodes should be stored in this when not in use to keep the glass membrane hydrated.

This is usually achieved with a cap or storage bottle which is filled with the solution and fits onto the end of the electrode.

6.3 How can I clean my electrode after it has been contaminated?

Between different buffers or samples the electrode should be rinsed with deionised water to remove residual traces. The electrode should not be wiped with a cloth or tissue as this can scratch or damage the membrane.

If the electrode has been in contact with an incompatible product like proteins or sulphides etc then a cleaning solution should be used. These are chemically designed to dissolve the solid precipitate which forms when the electrode reacts with these molecules.

If you are unsure what has caused the blockage the electrode can be cleaned in an ultrasonic bath with water or a 0.01 M solution of HCl.