Electrode Care & Maintenance Solutions

Introduction

pH is one of the most frequently and universally made measurements in science. Despite the number of people involved in pH measurement, the practical fundamentals governing it are not widely understood. The literature sometimes offers conflicting advice on how it is best measured and there is often uncertainty about the correct option available to deal with individual measurement applications. What is often not fully appreciated is that the vast majority of pH problems are related to the correct selection, care or maintenance of the electrode with particular emphasis on the reference electrode.

This brief technical note deals specifically with the correct choice of reference electrode filling solution and the compatibility of the filling solution with the sample being measured. It is important to keep two key considerations in mind as part of the selection process of the electrode filling solution. Firstly, the issue of the compatibility between the filling solution and the sample relates not only to direct pH measurement but also direct Ion and Redox measurement. It is also relevant to the use of all three sensors when performing potentiometric titrations. Secondly, the direct experience of the analyst, the operating instructions of the electrode or the detail contained within the test method being followed, may be of most value in the selection of the correct filling solution.

Correct choice of Electrode Filling Solution (Electrolyte)

A good electrolyte must fulfil a number of conditions. The equitransference of the cation/anion combination should be as close as possible to being equimobile, have constant chloride activity, be of high electrical conductance and as non-chemically reactive as possible.

Concentrated or saturated Potassium Chloride (KCl) fulfils all of these conditions to a greater or lesser extent and is the filling solution of choice in either potentiometric titrations or direct pH, redox or ion measurements where silver/silver chloride or calomel reference electrodes are used.

However, saturated KCl is only sparingly soluble below 20˚C, so if the measurements are carried out below this temperature weaker concentrations of this salt needs to be used. By way of example, 3.5M KCl remains in solution down to 15˚C and 2M KCl will remain in solution down to -5˚C. However, the lower the concentration of KCl the higher the liquid junction potential error that will arise in the measurement. For work at very low temperatures, 1.5M KCl dissolved in equal volumes of water and glycerin can be used. (KCl does not crystalize out of solution in this mixture until the temperature reaches -30˚C). This mixture will introduce even greater liquid junction errors.

The use of KCl in any concentration may be problematic in the following situations:

1. The following ions can react with Cl^- to form insoluble precipitates that block the diaphragm, Hg^{++}, Cu^{++}, Ag^+, Pb^{++} In such cases, a double junction electrode must be used with the outer chamber containing either Potassium Nitrate or Ammonium Sulphate at various concentrations. However, the potassium may also react with anions like Perchlorate (ClO^-_4) to form Potassium Perchlorate ($KClO_4$) which is sparingly soluble. In this situation Ammonium Sulfate can also be used as the filling solution in the outer chamber.
2. Some electrode manufacturers recommend the use of 3M KCl or 4M KCl saturated with Silver Chloride (AgCl) as the filling solution of choice. In this instance silver may react with several halides including bromides or iodides or may react with cyanides. Most importantly, silver may also react with sulfide which manifests itself in blackening of the diaphragm due to blockage. There may also be ingress of the sulfide into the electrode which will cause poisoning of the reference system, as well as high false liquid junction potentials. In this instance, silver free KCl can be used either as a primary electrolyte or in the outer junction of a double junction electrode.

3 2M Potassium Nitrate (KNO_3) + 0.001M Potassium Chloride may be used specifically for measurement of samples containing silver halides or used for argentimetric titrations where silver billet electrodes are used.

4 For pH measurement or titration in non-aqueous media or organic solvents, Lithium Chloride in Ethanol, Methanol, Isopropanol or Glacial Acetic Acid must be used as a filling solution in both the inner and outer chamber.

These hints are for guidance purposes and will help in the majority of applications. However, such hints can never be exhaustive or sufficiently comprehensive to cover all types of samples encountered.

Electrode Filling Solutions

Product No.	Description	Pack Size
EFS3005	3M Potassium Chloride (KCL), free from Silver ion	50ml
EFS3	3M Potassium Chloride (KCl), free from Silver ion	100ml
EFS3-250ML	3M Potassium Chloride (KCl), free from Silver ion	250ml
EFS35	3M Potassium Chloride (KCl), free from Silver ion	500ml
EFS301	3M Potassium Chloride (KCl), free from Silver ion	1L
EFS351	3.5M Potassium Chloride (KCl) free from Silver ion	100ml
EFS3511	3.5M Potassium Chloride (KCl) free from Silver ion	1L
EFS35AC	3.5M Potassium Chloride (KCl), saturated with AgCl	100ml
EFS35AC5	3.5M Potassium Chloride (KCl), saturated with AgCl	500ml
EFS381	3.8M Potassium Chloride (KCl), free from Silver ion	100ml
EFS3810	3.8M Potassium Chloride (KCl) free from Silver ion	1L
EFS4	4M Potassium Chloride (KCl), free from Silver ion	100ml
LKCL	Saturated Potassium (KCl), free from Silver ion	100ml
LKCL1	Saturated Potassium (KCl), free from Silver ion	1L
EFS3AC	3M Potassium Chloride (KCl), saturated with AgCl	100ml
EFS3AC-250ML	3M Potassium Chloride (KCl), saturated with AgCl	250ml
EFS3AC5	3M Potassium Chloride (KCl), saturated with AgCl	500ml
EFS4AC	4M Potassium Chloride (KCl), saturated with AgCl	100ml
EFSPS	Saturated Potassium Sulphate K_2SO_4	100ml
EFS2AS	Double Junction Bridge Solution 2M Ammonium Sulphate$(NH_4)_2SO_4$	100ml
EFS2-250ML	Double Junction Bridge Solution 2M Ammonium Sulphate$(NH_4)_2SO_4$	250ml
EFSAMO1	Ammonia	100ml
EFS01AS	Double Junction Bridge Solution 0.1M Ammonium Sulphate	100ml
EFSKNO	Double Junction Bridge Solution 10% w/v Potassium Nitrate	100ml
EFSLICL	Non-Aqueous Filling Solution; 1M Lithium Chloride (LiCl), dissolved in isopropanol	100ml
EFSLIET	Non-Aqueous Filling Solution; 1M Lithium Chloride (LiCl), dissolved in ethanol	100ml
EFSLIGA	Non-Aqueous Filling Solution; 1M lithium Chloride (LiCl), dissolved in glacial acetic acid	100ml
EFSDO	Dissolved Oxygen Electrolyte	100ml
EFSLIAPP	Low Ionic Strength Applications	100ml
EFSNACLO4	Saturated Sodium Perchlorate in Glacial Acetic Acid	100ml
EFSBR5	Preparation Cell Electrolyte for ASTM D1492 (Bromine)	5L

Electrode Cleaning Solutions

Designed to extend the useful life of your PH electrode.

Product No.	Description	Pack Size
ECS1	(Pepsin/Hydrochloric Acid) for removal of proteins	100ml
ECS-250ML	(Pepsin/Hydrochloric Acid) for removal of proteins	250ml
ECS	(Pepsin/Hydrochloric Acid) for removal of proteins	500ml
ECSF	(Pepsin/Hydrochloric Acid) for removal of proteins	1L
IECS	Inorganic (Thiourea/Hydrochloric Acid); for removal of sulphide	100ml
IECS5	Inorganic (Thiourea/Hydrochloric Acid); for removal of sulphide	500ml
IECS1	Inorganic (Thiourea/Hydrochloric Acid); for removal of sulphide	1L
OECS1	Organic Cleaning Solutions	100ml
OECS	Organic Cleaning Solutions	500ml
OECS5	Organic Cleaning Solutions	5L
ERS	Electrode Regeneration Solution	100ml
ECHPS	Rinse Solution, High Purity Water for Rinsing Electrodes	500ml
ERSS5	Electrode Rinse Solution	500ml

Electrode Storage Solutions

Product No.	Description	Pack Size
ESS001	pH Electrode Storage Solution	100ml
ESS5	pH Electrode Storage Solution	500ml
ESS01	pH Electrode Storage Solution	1L
ESS05	pH Electrode Storage Solution	5L

Electrode Care & Maintenance Kit

This is a unique Kit designed to help calibrate, clean and extend the useful life of your pH electrodes.

Contents include:

- pH buffers in twin neck bottles - 1 x 500ml each of pH 4.00/7.00/10.00 @ 20°C
- Electrode Storage Solution - 1 x 500ml
- Electrode Cleaning Solution - 1 x 100ml each of Biological, Organic and Inorganic Solutions
- Filling Solution 1 x 100ml each of 3M KCl/AgCl and 4M KCl
- Pipettes (2)
- Regeneration Solution - 1 x 100ml
- Instruction card and GLP Log Book

Product No.	Description	Pack Size
RCMK1	REAGECARE pH Electrode Care & Maintenance Kit	Kit