

Reference Electrode Potentials

Introduction:

The three most commonly used Reference Electrodes are the Calomel, Silver/Silver Chloride and Copper Sulphate electrode systems. These are used for all potential difference measurements (mV) in electrochemistry - the most common being pH, REDOX and Ion Analysis.

They all provide a perfectly stable potential for these measurements however they do have advantages and disadvantages some of which can be summarised as follows.

Calomel References:

Historically the most commonly used electrode so reference texts often use data produced using this half-cell. The filling solution is just saturated Potassium Chloride which is easy to prepare. If crystallised out in the junction material it is easily dissolved in water to restore the electrode performance.

The main disadvantage is that the Calomel electrode contains Mercury and Mercury II Chloride which is hazardous and harmful to the environment and small organisms. Responsible disposal is therefore important which can be expensive and inconvenient.



Silver/Silver Chloride References:

These have become the most commonly used systems as they are cheap to manufacture and don't have the environmental issues of the Calomel units. They are also more easily miniaturised which is beneficial when making combination electrodes.

The filling solution contains Saturated AgCl and KCl and is generally more expensive. The Silver Chloride can deposit in the junction causing irreparable damage. Once deposited it cannot be redissolved like KCl. The main symptoms are increased junction potentials and a black appearance of the once white junction material.



The Calomel electrode is generally not used above 50 degrees C which can be a disadvantage. The Ag/AgCl reference however is more stable at higher temperatures and therefore can be reliable up to around 80 degrees C.

Copper Sulphate References:

These reference electrodes are quite distinctive as the filling solution is saturated Copper II Sulphate which is a vibrant blue colour. The filling solution often contains undissolved blue crystals of Copper Sulphate. This is normal and indicates that the solution is saturated.

These references were commonly used in marine applications related mainly to corrosion and Cathodic Disbondment (CD testing). They have the advantage of having a good resistance to fouling and reference blockages which can be a disadvantage of Ag/AgCl electrodes. They are also free of Mercury so do not represent a hazard to the local environment.



Typical Reference Electrode Potentials:

The offset potentials of reference electrodes vary as they depend on parameters such as Junction types, fill solution concentration and materials used in manufacture. However, in general, the three different electrode types have distinctive potentials. In the literature these are generally reported when compared to the Standard Hydrogen Electrode (SHE).

A reference electrode is half of the measurement cell which is completed by a sensing electrode. In this case the SHE but normally these are pH, REDOX or ISEs.

Reference Type	Typical potential when compared to the SHE
Calomel (Hg/HgCl ₂)	+244mV
Silver/Silver Chloride (Ag/AgCl)	+214mV
Copper Sulphate (Cu/CuSO ₄)	+314mV

The actual potentials vs the SHE are not critical in themselves however you will see that there can be a difference in the mV reading which could be as much as 100mV.

If you are comparing your data to that quoted in the literature, it is therefore important to make sure the reference is the same.

When measuring pH or Ions this difference is eliminated by calibrating the electrode pair in standard solutions. However, if the results are expressed in mV such as REDOX, Hull Potential or Cathodic Disbondment the reference type needs to be noted to ensure you are comparing like with like.

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Calomel Reference
Electrode



Silver/Silver Chloride
Reference Electrode



Copper Sulphate
Reference Electrode

