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pHOenix Co.

**Education Series
Reference Electrode Guide**



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Reference Electrode Guide

The purpose of this article is to educate the user about one of the most important aspects of electrode measurements - the Reference Electrode. Most difficulties experienced while performing measurements with electrodes can be traced to the reference electrode, and more specifically, to the reference electrode's liquid junction. Therefore, a greater knowledge of the role the reference electrode plays is of great benefit to the user. We will discuss the various types of reference electrodes, the components which make up the reference electrodes, and their various relative strengths and weaknesses so you can make an informed decision as to which reference electrode type is right for your application.

We will start by defining the purpose of the reference electrode. This purpose is to complete the electrical circuit necessary for an electrochemical measurement by providing the second electrode of a complete electrode cell whose total potential is measured. The reference electrode achieves this by providing contact with the sample through its liquid junction. For a reference electrode to be useful, it must provide both a stable and reproducible potential to which the indicating electrode potential can be compared.

Reference Electrode Construction

Figure 1

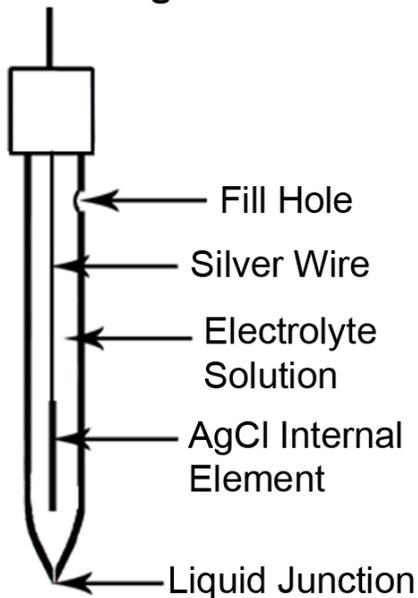


Figure 1 to the left shows the various parts of a typical reference electrode.

The typical reference electrode consists of an internal element, normally silver-silver chloride, surrounded by an electrolyte-containing filling solution (commonly KCl, saturated with AgCl) which is contained in either a glass or plastic body salt bridge, which terminates at the liquid junction.

It is important that the internal element remain wet and surrounded by the reference electrolyte filling solution. This is why VL-PC ships all its reference electrodes pre-filled with reference filling solution. To prevent leakage of the filling solution through the fill hole during shipment, the fill hole is sealed with either tape or a rubber grommet. This seal must be removed prior to use. If this seal is not removed, as the fill solution leaks out of the liquid junction, a vacuum will be created inside the electrode until the fill solution can no longer flow out of the electrode. This can result in drifting or unstable readings.

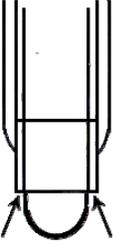
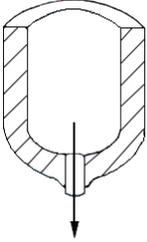
Our reference electrodes are also shipped with a cap containing reference fill solution covering the liquid junction. Like the internal element, the liquid junction needs to be kept wet in order for the electrode to function properly.

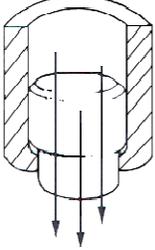
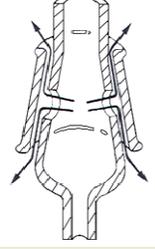
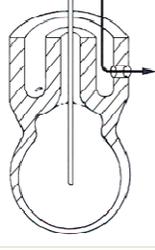
Liquid Junctions

The liquid junction allows the leakage of reference electrolyte filling solution into the sample, thereby completing the electrical circuit needed for potentiometric measurements. VL-PC can manufacture reference electrodes in various configurations and from various materials. There are a variety of liquid junction styles and materials to choose from. Keep in mind that there is no "universal" liquid junction. The differences between the various junction types are mainly the potentials generated at the liquid junction-sample interface, and the flow rate of reference filling solution through the liquid junction into the sample. The choice of liquid junction type is mostly application dependent.

There are two basic classes of liquid junctions. The first, is referred to as a "flowing" junction. This class of liquid junction allows the electrolyte in its entirety (liquid/gel and all) to make contact with the sample through the junction (see Glass Sleeve and Open Aperture examples below). Liquid junctions of this type have moderate to high flow rates, provide low resistance and low junction potentials, but have a higher degree of sample contamination. The second class of liquid junctions are referred to as a "Diffusion" junction (see Annular Ceramic, Ceramic Wick, and Teflon examples below). This class of liquid junction allows only the ions of the electrolyte to pass through the junction and into the test sample. Diffusion type liquid junctions exhibit lower flow rates and less sample contamination, but are more readily clogged. Table 1 below describes the various reference liquid junctions VL-PC offers and which applications for which they are suitable .

Table 1 The Various Types of Liquid Junctions

	<p>Description: The annular ceramic junction is made by wedging a thin layer of ceramic between the outer body and inner body of the reference chamber. The ceramic itself has a small pore size, therefor it exhibits a low flow rate, extending the time between refilling of the reference electrolyte.</p> <p>This type of liquid junction are suitable for most general laboratory type applications.</p> <p>The principle drawback of this style is that the liquid junction itself is difficult to clean, once it has become contaminated/fouled. Careful selection of the reference electrolyte can help reduce/eliminate the fouling effect.</p>
<p>Annular Ceramic</p> 	<p>Description: The ceramic wick junction is made by inserting a ceramic wick (also called a frit) through the tip/end of the reference chamber. The ceramic wick shares many characteristics with the annular ceramic style liquid junction. The ceramic wick has a small pore size (although various pore sizes are available upon special request), and therefor, a slow flow rate. This liquid junction type also is difficult to clean if it becomes fouled. Again, careful selection of the reference electrolyte can help mitigate/eliminate the fouling effect.</p> <p>Ceramic Wick</p>

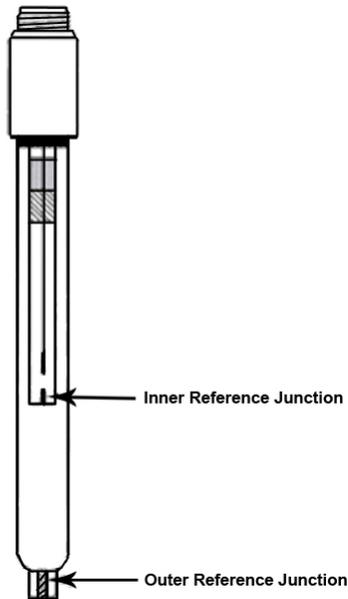
	<p>Description: This liquid junction is made by press fitting a plug of teflon into the tip of the reference electrode. Teflon is a very versatile liquid junction material, as it can be used in either a flowing reference design (with a liquid reference electrolyte, such as in laboratory style electrodes), or in a diffusion style liquid junction (with a gelled electrolyte). Teflon liquid junctions are prominently found in industrial application electrodes. When combined with a polymer gel reference electrolyte, the hydrophobic nature of teflon helps prevent contamination of the liquid junction, while its large pore size make for low junction potentials, and the ability to more rapidly equilibrate to pressure changes in those applications where the environment is dynamic in nature.</p>
<p>P.T.F.E. (Teflon)</p>	
	<p>Description: This liquid junction type is made by drilling a small hole in the side of the reference electrode. A movable, tapered ground glass "sleeve" envelops the outer body of the reference electrode. This sleeve can be moved up the electrode body to fully expose the hole, allowing quick draining of the reference electrolyte for cleaning, and moved down to cover the hole for operational use. This style of liquid junction exhibits an extremely high flow rate. As such, it offers highly stable and very low junction potentials. The very fast flow rate of these types of reference electrodes requires frequent refilling of the reference electrolyte, however, and sample contamination may be of concern for certain applications. This style of reference electrodes are generally found in laboratory applications, where accuracy is paramount.</p>
<p>Glass Sleeve</p>	
	<p>Description: This liquid junction is made by simply drilling a hole in the side of the reference electrode. The reference electrolyte must be gelled in some fashion to prevent overly rapid depletion of reference electrolyte. The reference electrolyte gel is completely exposed to the sample. The open aperture style liquid junction is typically used in applications having high solids content and in suspensions/emulsions. The open aperture junction is also beneficial in the monitoring of precipitation reactions, which can easily clog/foul other liquid junction styles which have a physical, porous salt bridge.</p>
<p>Open Aperture</p>	

Contamination Effects

As stated earlier, the Silver-Silver chloride reference element is the reference element of choice, with a potassium chloride solution saturated with Silver chloride used as the reference electrolyte fill. The KCl solution is saturated with AgCl to prevent incidental stripping of the AgCl off of the Silver wire (the reference internal element) to dissolve into the KCl reference electrolyte solution.

But what do we do if the sample we wish to test would become contaminated if it were to come into contact with Silver ions (such as in the food industry)? Or what if the sample contains silver ions, and we don't wish to expose the sample to a reference electrolyte containing chloride ions?

Double Junction Reference Electrode



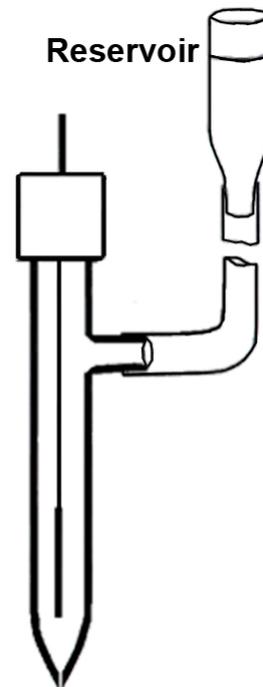
This problem is solved by adding a second salt bridge, or junction to the reference electrode to insulate the inner Silver-Silver chloride reference element from the sample. This secondary salt bridge can then be filled with a reference electrolyte solution which does not contain a contaminant to the sample. In the case of a sample containing Silver ions, for example, one might choose a saturated Potassium nitrate (KNO_3) solution as the reference electrolyte.

Side Arm Reference with Fill Solution Reservoir

Contamination of the internal reference element by the sample is also possible if the level of the reference electrode's filling solution is not properly maintained. The desired flow of filling solution from the reference chamber into the sample is only possible if there is a positive head pressure, that is, the level of filling solution must be higher than that of the sample. If the sample level is higher than that of the level of reference filling solution, the normal direction of flow can reverse, with the sample flowing into the reference chamber. At the minimum, this can result in the formation of unstable potentials. Extended sample exposure to the internal reference element can lead to contamination/fouling of the internal reference element itself. If this happens, the reference electrode must be replaced.

For this reason, VL-PC offers reference electrodes with a built-in side arm, for maintaining the positive head pressure needed for proper reference electrode function. Pictured to the right, is an example of how one can connect a reservoir, filled with reference electrolyte filling solution, to the reference electrode to maintain positive head pressure.

This type of setup is common where long term measurements are needed, but daily electrode maintenance is not possible or convenient.



Liquid Junction Potentials

When a reference electrode is placed into the sample, a potential develops at the junction where the reference filling solution and sample meet - the liquid junction. This potential develops because the reference fill solution is of different composition than the sample. The liquid junction is designed to allow interdiffusion of ions between the reference filling solution and the sample. However, different ions diffuse at different rates, so the electrical charge they carry will move unequally across the junction. Hence, the formation of the reference junction potential. By careful selection of the liquid junction material and the reference filling solution used, we can control both the magnitude and stability of the reference junction potential.

Table 1 above will serve as a guide as to which junction material type is appropriate for your application. The next section will discuss in more detail our choice of reference fill solution.

Reference Filling Solutions

The ideal reference filling solution for any particular application should meet the following requirements:

- The filling solution's electrolyte should neither react with, nor contaminate the sample.
- The filling solution should provide the dominant ions (in concentration) present at the liquid junction interface.
- The diffusion rates of both the cations and anions of the filling solution's electrolyte should be as close to equal as possible.

We have already mentioned an example of the 1st requirement - the example of the typical reference filling solution of KCl reacting with a sample containing Silver to form silver chloride. The second requirement is readily accomplished by simply making the fill solution either saturated, or sufficiently concentrated with the electrolyte of choice. The third requirement is accomplished by choosing a reference fill solution whose electrolyte provides equal transference of the positive and negative charges moving across the liquid junction.

The ability of an ion to carry an electrical charge can be compared based on its ionic equivalent conductance (λ^0 , mho-cm/equivalent/liter). Below is a table of varying ions and their equivalent conductance in various solutions.

Cation	Aqueous	Methanol	Ethanol
Ag ⁺	61.9	---	17.9
Ba ⁺²	63.6	62.0	---
Ca ⁺²	59.5	61.0	---
Cu ⁺²	53.6	---	---
H ⁺	349.8	141.8	57.4
K ⁺	73.5	52.4	22.0
Li ⁺	38.7	39.8	15.0
Mg ⁺²	53.1	59.0	---
Na ⁺²	50.1	45.9	18.9

NH_4^+	73.5	57.9	19.6
$(\text{CH}_3)_4\text{N}^+$	44.9	70.1	28.3
$(\text{C}_2\text{H}_5)(\text{CH}_3)_3\text{N}^+$	40.8	---	---
$(\text{C}_4\text{Hg})(\text{CH}_3)_3\text{N}^+$	33.6	---	---
$(\text{C}_2\text{H}_5)_4\text{N}^+$	32.7	60.4	27.8
$(\text{C}_3\text{H}_7)_4\text{N}^+$	23.4	46.1	---
$(n\text{-C}_4\text{H}_9)_4\text{N}^+$	19.5	39.1	---
<u>Anion</u>			
Br^-	78.14	56.4	26.0
Cl^-	76.4	51.2	24.3
CO_3^{-2}	69.3	---	---
ClO_4^-	67.3	70.1	33.5
F^-	55.4	---	---
HCO_3^-	44.5	---	---
I^-	76.8	62.7	28.8
NO_3^-	71.4	60.5	28.0
OH^-	198.6	---	---
SO_4^{-2}	80.0	---	---
SCN^-	66.0	60.8	29.7
Acetate ⁻	40.9	53.0	---
Benzoate ⁻	32.4		
N-Butyrate ⁻	32.6		
Oxalate ⁻²	74.2		
Picrate ⁻	30.4	47.0	26.3
Propionate ⁻	35.8	---	21.0
* From Parsons, "Handbook of Electrochemical Constants," Butterworth, London, 1959, and L. Meites, "Handbook of Analytical Chemistry," McGraw-Hill, New York, 1973.			

Looking at this table, one can see why KCl is a very popular reference electrolyte fill solution. Potassium has a limiting equivalent conductance of 73.5, while Chloride has a limiting equivalent conductance of 76.4. Take note of

the limiting equivalent conductance values for H^+ and OH^- . They are much higher than the values for most other ions. This is what makes achieving equitransference in strong acids and strong bases difficult, and is often the cause for the long response times encountered when measuring these samples.

Effects of changing the reference fill solution

When the reference filling solution of a reference electrode is changed, the potential developed at the fill solution-internal reference element interface will change as well. This new potential may be less stable and/or more sensitive to temperature changes than the previous fill solution, so take careful note of response times when using a new reference fill solution for the first time. Also, be aware that this new potential may take quite some time to establish itself, so allowing a reference electrode to stand overnight filled with its new reference filling solution is a good practice when changing out fill solutions. It is for these reasons that in practice, most people do not change out the reference fill solution, but simply purchase separate reference electrodes, with each reference electrode being dedicated to a single reference fill solution.

Crystallization

Experienced users of reference electrodes have seen many times over the formation of crystals at the bottom end of their electrodes, and know them for what they are - simply the salt crystals of the electrolyte solution used in the reference electrode. To novice users, however, this at first may seem to be some form of contamination, but it is not. Most reference electrolyte filling solutions are saturated salt solutions. For various reasons, such as water evaporating from the fill solution, or a drop in temperature, these salts will fall out of solution and form crystals, which naturally settle to the bottom of the electrode. These salt crystals will not, up to a point, interfere with the electrode's performance. The crystals, actually serve a purpose to us. They ensure the filling solution maintains saturation. However, these crystals can, over periods of time, become packed together so tightly that they hinder the proper flow of reference filling solution through the junction. This can be easily remedied, by draining the reference electrode of its reference fill solution and refilling it with distilled water. This will allow the salt crystals to dissolve into the distilled water, which can then be drained and replaced with the reference filling solution once again. Note, sometimes, several rinsings with distilled water may be necessary to dissolve all the crystals.

Cleaning/Unclogging a Liquid Junction

If you are experiencing drift, jumpy, or readings requiring a long stabilization time, you may be experiencing the effects of a clogged liquid junction. The first cleaning method to try is that described above in the crystallization section. Simply drain the electrode of fill solution, rinse it several times with distilled water, and refill the electrode with its standard filling solution. If this doesn't improve the performance of the electrode, you can next try pulling a vacuum over the liquid junction (typically located at the tip of the electrode) to try and force the filling solution through the liquid junction. If your liquid junction remains clogged, more severe steps can be taken. The next step is to boil the liquid junction in a dilute KCl solution for 10 minutes. After 10 minutes, turn off the heat and allow the electrode to cool while immersed in the solution before the resuming of testing. The last step to try, if boiling is unsuccessful, is the physical, abrasive cleaning of the liquid junction itself. Place a piece of #600 emory paper on a flat surface and place a drop of water on the emory paper. Placing the liquid junction perpendicular to the emory paper, rotate the liquid junction in a circular fashion against the emory paper. Note, this cleaning method is to be used only as a last resort, as sanding the liquid junction will severely shorten the life of the reference electrode.