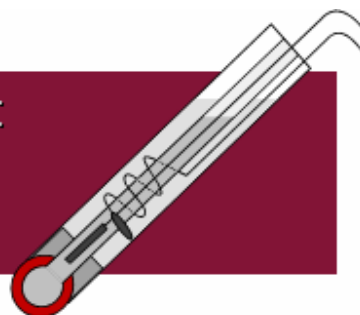


# Analytical Electrochemistry : Potentiometry

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## **Common Troubleshooting Tips:**

While understanding the underlying general concepts of potentiometry is a useful first step at becoming a regular "potentiometric practitioner", experience is also a great resource for effectively conducting these types of measurements. Through experience comes familiarity with common "problem areas" of this field. This page is intended to present some troubleshooting tips. It is not our intention to replace recommendations outlined in manufacturer literature.

Before specific discussion on common problem areas, the subtle nuance differences between efforts in calibration methods and quality control (QC) must be highlighted. Calibration and QC methods are complementary to one another and are often integrated into a method validation program that defines the overall reliability. Calibrations give analytical methods an initial quantitative starting point, whereas QC validates the developed calibration model.

Many classic questions arise, such as, "How often does calibration need to be performed?" and "What are some examples that require re-calibration?" QC should be performed on a daily basis in an industrial setting, if not more often. Various companies are required to maintain SOPs (standard operation procedures), among other validation protocol required for state and federal regulations. The generic answer to when the analyst should consider re-validating the method is when conditions change. Some examples of change include hardware, consumables (change in vendors and even a change in lots from the same vendor), sampling methods, and of-course if QC fails.

So, what are some of the specific concerns when using potentiometric electrodes? Faulty measurements, long response times, and unstable values can typically be traced back to problems at the liquid junction. One of the most important tasks in maintaining a trouble-free potentiometric analysis is electrode conditioning, more specifically "membrane conditioning" when using Ion-Selective Electrodes (ISE). In addition to providing selectivity through specific interactions, these membranes will also serve as salt bridges when an internal reference electrode setup is being used. This salt bridge is necessary to provide connection between the internal reference electrode and the unknown solution, and therefore these membranes must be maintained for proper use. The old adage of "an ounce of prevention is worth a pound of cure," justly applies here.

**Membrane Conditioning:** Initial conditioning is extremely important and commonly overlooked. For example, prior to using pH electrodes, the exterior surface of the glass membrane must be fully hydrated. Ion exchange at the hydrated glass surface then leads to the establishment of a potential across the membrane, its magnitude being determined by the concentration difference between the internal reference solution and the external analyte solution.

Routine maintenance of electrodes is also necessary. For combination electrodes containing a reference electrode separated from the external solution by a porous frit or plug, the level of internal electrolyte must be regulated appropriately. Proper operation requires that the drainage hole, typically located at the top of the electrode, be opened during measurements, allowing electrolyte solution to slowly flow through the porous junction into the external solution. The level of the internal fill solution should be kept above that of the measured analyte solution. One concern here is to avoid the species in the solution forming a precipitate with the exiting electrolyte species. To ensure that the sample solution does not alter critical parameters of the analyte solution, constant ionic strength buffers are frequently used. Electrodes with a second electrolyte junction (double junction) generally have longer lifetimes than those with a single junction.

**Matrix effects:** Matrix effects can have a substantial impact on the response function (e.g. sensitivity) of potentiometric electrodes. Standard addition methods are recommended for non-ideal solutions, such as lake-water sampling. Standard addition methods are recommended procedure for determining unknown analyte concentrations. Simple calibration might not account for response of background, or interfering species. Internal standard methods, used for compensating for variations in experimental parameters, are not widely used for potentiometric determinations, unless extensive sample preparation methods are necessary and one would want to account for sample loss during preparation.

### **Calibrations:**

- total ionic strength adjustor buffer (TISAB) to ensure standards and samples have similar ionic strength and to reduce interference from other ions
- calibration best performed with standards that bracket expected unknown concentration...especially if outside linear dynamic range
- standard addition – limited samples, high ionic strength, or complicated background – must be on linear part of calibration curve
- titrations – quantitative measurement of species concentration via addition of reagent that reacts with species of interest...~10x more precise than direct, but very time consuming

**Other On-line Resources:** For a more detailed trouble shooting guide (in PDF format) please visit [http://www.metrohm.co.uk/elcat\\_e\\_10\\_basic\\_pot.pdf](http://www.metrohm.co.uk/elcat_e_10_basic_pot.pdf). Common problems with pH glass electrodes are listed in Table 3. Metal electrode troubleshooting is presented in Table 5. Interfering ions for specific ISEs are listed in Table 6. Lastly, ISE troubleshooting tips are detailed in Table 7 of the above link.