There are a wide variety of analytical methods that are based on the use of electrochemical reactions or processes. Only a subset of all the electrochemical methods will be discussed herein. The simplest electrochemical cell has two electrodes. One of them is sensitive toward the analyte and is referred to as either the working or indicator electrode. The second electrode is referred to as the counter or reference electrode, with the potential of the working electrode measured relative to it. The most common reference electrode is comprised of a silver-silver chloride (Ag/AgCl) half-cell, with a fill solution that is saturated with KCl and AgCl (Figure 8).

$$\text{AgCl (s) + e}^- \rightleftharpoons \text{Ag(s) + Cl}^-\text{(sat)} \hspace{20px} E = +0.197\text{ V}$$

*Figure 8. Diagram of a silver-silver chloride reference electrode. (Figure from Analytical Chemistry 2.0, David Harvey, http://community.asdlib.org/activelearning-textbook/).*

The measurement uses a device known as a potentiostat, which is an electronic component that can run a three electrode cell. The potentiostat maintains the potential of the working electrode at a constant level with respect to the reference electrode. In some cases, it will be important that there be no current running through the reference electrode, which is achieved by having the system at a high impedance.

While a Ag/AgCl electrode is commonly used as a reference so that potentials are measured relative to it, for the purposes of the methods discussed herein, we will use the standard hydrogen electrode (SHE) as the reference electrode. Since the potential of the SHE is 0.00 Volts, this will allow us to use the numbers directly from a table of standard electrode potentials without having to correct for the potential of the reference electrode.