The easiest way to ensure 100% current efficiency is to hold the working electrode at a constant potential, chosen so that the analyte reacts completely without simultaneously oxidizing or reducing an interfering species. As electrolysis progresses the analyte’s concentration decreases, as does the current. The resulting current-versus-time profile for controlled-potential coulometry is shown in Figure 11.27. Integrating the area under the curve (equation 11.27) from \( t = 0 \) to \( t = t_e \) gives the total charge. In this section we consider the experimental parameters and instrumentation needed to develop a controlled-potential coulometric method of analysis.

![Figure 11.27](image)

**Figure 11.27** Current versus time for a controlled-potential coulometric analysis. The measured current is shown by the red curve. The integrated area under the curve, shown in blue, is the total charge.

### Selecting a Constant Potential

To see how an appropriate potential for the working electrode is selected, let’s develop a constant-potential coulometric method for Cu\(^{2+}\) based on its reduction to copper metal at a Pt working electrode.

\[
\text{\ce{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}} \tag{11.28}
\]

Figure 11.28 shows a ladder diagram for an aqueous solution of Cu\(^{2+}\). From the ladder diagram we know that reaction 11.28 is favored when the working electrode’s potential is more negative than +0.342 V versus the standard hydrogen electrode. To ensure a 100% current efficiency, however, the potential must be sufficiently more positive than +0.000 V so that the reduction of H\(_3\)O\(^+\) to H\(_2\) does not contribute significantly to the total current flowing through the electrochemical cell.
Figure 11.28 Ladder diagram for an aqueous solution of Cu\(^{2+}\) showing steps for the reductions of O\(_2\) to H\(_2\)O, of Cu\(^{2+}\) to Cu, and of H\(_3\)O\(^+\) to H\(_2\). For each step, the oxidized species is in blue and the reduced species is in red.

We can use the Nernst equation for reaction 11.28 to estimate the minimum potential for quantitatively reducing Cu\(^{2+}\).

\[ E = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - \frac{0.05916}{2}\log\frac{1}{[\text{Cu}^{2+}]} \tag{11.29} \]

Note

So why are we using the concentration of Cu\(^{2+}\) in equation 11.29 instead of its activity? In potentiometry we write the Nernst equation using activity because we use \(E_{\text{cell}}\) to determine the amount of analyte in the sample. Here we are using the Nernst equation to design the analysis. The amount of analyte is given by the total charge, not the applied potential.

If we define a quantitative electrolysis as one in which we reduce 99.99% of Cu\(^{2+}\) to Cu, then the concentration of Cu\(^{2+}\) at \(t_0\) is

\[ [\text{Cu}^{2+}]_{t_0} = 0.0001 \times [\text{Cu}^{2+}]_0 \tag{11.30} \]

where \([\text{Cu}^{2+}]_0\) is the initial concentration of Cu\(^{2+}\) in the sample. Substituting equation 11.30 into equation 11.29 allows us to calculate the desired potential.

\[ E = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - \frac{0.05916}{2}\log\frac{1}{0.0001 \times [\text{Cu}^{2+}]_0} \]

If the initial concentration of Cu\(^{2+}\) is \(1.00 \times 10^{-4}\) M, for example, then the working electrode’s potential must be more negative than +0.105 V to quantitatively reduce Cu\(^{2+}\) to Cu. Note that at this potential H\(_3\)O\(^+\) is not reduced to H\(_2\), maintaining 100% current efficiency.

Note
Many controlled-potential coulometric methods for Cu$^{2+}$ use a potential that is negative relative to the standard hydrogen electrode—see, for example, Rechnitz, G. A. *Controlled-Potential Analysis*, Macmillan: New York, 1963, p.49.

Based on the ladder diagram in Figure 11.28 you might expect that applying a potential <0.000 V will partially reduce H$_3$O$^+$ to H$_2$, resulting in a current efficiency that is less than 100%. The reason we can use such a negative potential is that the reaction rate for the reduction of H$_3$O$^+$ to H$_2$ at is very slow at a Pt electrode. This results in a significant overpotential—the need to apply a more positive or a more negative potential than predicted by thermodynamics—that shifts $E^0$ for the H$_3$O$^+/H_2$ redox couple to a more negative value.

### Minimizing Electrolysis Time

In controlled-potential coulometry, as shown in Figure 11.27, the current decreases over time. As a result, the rate of electrolysis—recall from Section 11A that current is a measure of rate—becomes slower and an exhaustive electrolysis of the analyte may require a long time. Because time is an important consideration when choosing and designing analytical methods, we need to consider the factors affecting the analysis time.

We can approximate the change in current as a function of time in Figure 11.27 by an exponential decay; thus, the current at time $t$ is

$$i = i_0 e^{-kt} \tag{11.31}$$

where $i_0$ is the current at $t = 0$ and $k$ is a rate constant that is directly proportional to the area of the working electrode and the rate of stirring, and that is inversely proportional to the volume of solution. (Problem11.16 asks you to explain why a larger surface area, a faster stirring rate, and a smaller volume leads to a shorter analysis time.) For an exhaustive electrolysis in which we oxidize or reduce 99.99% of the analyte, the current at the end of the analysis, $t_e$, is

$$i \leq 0.0001 \times i_0 \tag{11.32}$$

Substituting equation 11.32 into equation 11.31 and solving for $t_e$ gives the minimum time for an exhaustive electrolysis as

$$t_e = \frac{9.21}{k} \ln(0.0001)$$

From this equation we see that a larger value for $k$ reduces the analysis time. For this reason we usually carry out a controlled-potential coulometric analysis in a small volume electrochemical cell, using an electrode with a large surface area, and with a high stirring rate. A quantitative electrolysis typically requires approximately 30–60 min, although shorter or longer times are possible.

### Instrumentation

A three-electrode potentiostat is used to set the potential in controlled-potential coulometry. The working electrodes is usually one of two types: a cylindrical Pt electrode manufactured from platinum-gauze (Figure 11.29), or a Hg pool electrode. The large overpotential for the reduction of H$_3$O$^+$ at Hg makes it the electrode of choice for an analyte requiring a negative potential. For example, a potential more negative than –1 V versus the SHE is feasible at a Hg electrode—but
not at a Pt electrode—even in a very acidic solution. Because mercury is easily oxidized, it is less useful if we need to maintain a potential that is positive with respect to the SHE. Platinum is the working electrode of choice when we need to apply a positive potential.

Note

Figure 11.5 shows an example of a manual three-electrode potentiostat. Although a modern potentiostat uses very different circuitry, you can use Figure 11.5 and the accompanying discussion to understand how we can use the three electrodes to set the potential and monitor the current.

![Cylindrical Pt-gauze electrode](image)

**Figure 11.29** Example of a cylindrical Pt-gauze electrode for controlled-potential coulometry. The electrode shown here has a diameter of 13 mm and a height of 48 mm, and is fashioned using Pt wire with a diameter of approximately 0.15 mm. The electrode’s surface has 360 openings/cm² and a total surface area of approximately 40 cm².

The auxiliary electrode, which is often a Pt wire, is separated by a salt bridge from the analytical solution. This is necessary to prevent the electrolysis products generated at the auxiliary electrode from reacting with the analyte and interfering in the analysis. A saturated calomel or Ag/AgCl electrode serves as the reference electrode.

The other essential instrumental need for controlled-potential coulometry is a means for determining the total charge. One method is to monitor the current as a function of time and determine the area under the curve, as shown in Figure 11.27. Modern instruments use electronic integration to monitor charge as a function of time. The total charge at the end of the electrolysis is read directly from a digital readout.
Electrogravimetry

If the product of controlled-potential coulometry forms a deposit on the working electrode, then we can use the change in the electrode’s mass as the analytical signal. For example, if we apply a potential that reduces $\text{Cu}^{2+}$ to $\text{Cu}$ at a Pt working electrode, the difference in the electrode’s mass before and after electrolysis is a direct measurement of the amount of copper in the sample. We call an analytical technique that uses mass as a signal a gravimetric technique; thus, we call this electrogravimetry.

Note

For a review of other gravimetric techniques, see Chapter 8.