In this chapter we introduced three electrochemical methods of analysis: potentiometry, coulometry, and voltammetry. In potentiometry we measure the potential of an indicator electrode without allowing any significant current to pass through the electrochemical cell. In principle we can use the Nernst equation to calculate the analyte’s activity—junction potentials, however, require that we standardize the electrode.

There are two broad classes of potentiometric electrodes: metallic electrodes and membrane electrodes. The potential of a metallic electrode is the result of a redox reaction at the electrode’s surface. An electrode of the first kind responds to the concentration of its cation in solution; thus, the potential of a Ag wire is determined by the activity of Ag\(^+\) in solution. If another species is in equilibrium with the metal ion, the electrode’s potential also responds to the concentration of that species. For example, the potential of a Ag wire in a solution of Cl\(^-\) responds to the concentration of Cl\(^-\) because the relative concentrations of Ag\(^+\) and Cl\(^-\) are fixed by the solubility product for AgCl. We call this an electrode of the second kind.

The potential of a membrane electrode is determined by a difference in the composition of the solution on each side of the membrane. Electrodes using a glass membrane respond to ions that bind to negatively charged sites on the membrane’s surface. A pH electrode is one example of a glass membrane electrode. Other kinds of membrane electrodes include those using insoluble crystalline solids or liquid ion-exchangers incorporated into a hydrophobic membrane. The F\(^-\) ion-selective electrode, which uses a single crystal of LaF\(_3\) as the ion-selective membrane, is an example of a solid-state electrode. The Ca\(^{2+}\) ion-selective electrode, in which the chelating di-(n-decyl)phosphate is immobilized in a PVC membrane, is an example of a liquid-based ion-selective electrode.

Potentiometric electrodes can be designed to respond to molecules by using a chemical reaction that produces an ion whose concentration can be determined using a traditional ion-selective electrode. A gas-sensing electrode, for example, include a gas permeable membrane that isolates the ion-selective electrode from the gas. When the gas diffuses across the membrane it alters the composition of the inner solution, which is monitored with an ion-selective electrode. An enzyme electrodes operate in the same way.

Coulometric methods are based on Faraday’s law that the total charge or current passed during an electrolysis is proportional to the amount of reactants and products in the redox reaction. If the electrolysis is 100% efficient—meaning that only the analyte is oxidized or reduced—then we can use the total charge or current to determine the amount of analyte in a sample. In controlled-potential coulometry we apply a constant potential and measure the resulting current as a function of time. In controlled-current coulometry the current is held constant and we measure the time required to completely oxidize or reduce the analyte.

In voltammetry we measure the current in an electrochemical cell as a function of the applied potential. There are several different voltammetric methods that differ in terms of the type of working electrode, how we apply the potential, and whether we include convection (stirring) as a means for transporting of material to the working electrode.

Polarography is a voltammetric technique that uses a mercury electrode and an unstirred solution. Normal polarography uses a dropping mercury electrode, or a static mercury drop electrode, and a linear potential scan. Other forms of polarography include normal pulse polarography, differential pulse polarography, staircase polarography, and square-wave polarography, all of which use a series of potential pulses.
In hydrodynamic voltammetry the solution is stirred using either a magnetic stir bar or by rotating the electrode. Because the solution is stirred a dropping mercury electrode can not be used; instead we use a solid electrode. Both linear potential scans and potential pulses can be applied.

In stripping voltammetry the analyte is first deposited on the electrode, usually as the result of an oxidation or reduction reaction. The potential is then scanned, either linearly or by using potential pulses, in a direction that removes the analyte by a reduction or oxidation reaction.

Amperometry is a voltammetric method in which we apply a constant potential to the electrode and measure the resulting current. Amperometry is most often used in the construction of chemical sensors for the quantitative analysis of single analytes. One important example is the Clark O₂ electrode, which responds to the concentration of dissolved O₂ in solutions such as blood and water.

11.5.1 Key Terms

- amalgam
- amperometry
- anode
- anodic current
- asymmetry potential
- auxiliary electrode
- cathode
- cathodic current
- charging current
- controlled-current coulometry
- controlled-potential coulometry
- convection
- coulometric titrations
- coulometry
- counter electrode
- current efficiency
- cyclic voltammetry
- diffusion
- diffusion layer
- dropping mercury electrode
- electrical double layer
- electrochemically irreversible
- electrochemically reversible
References


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