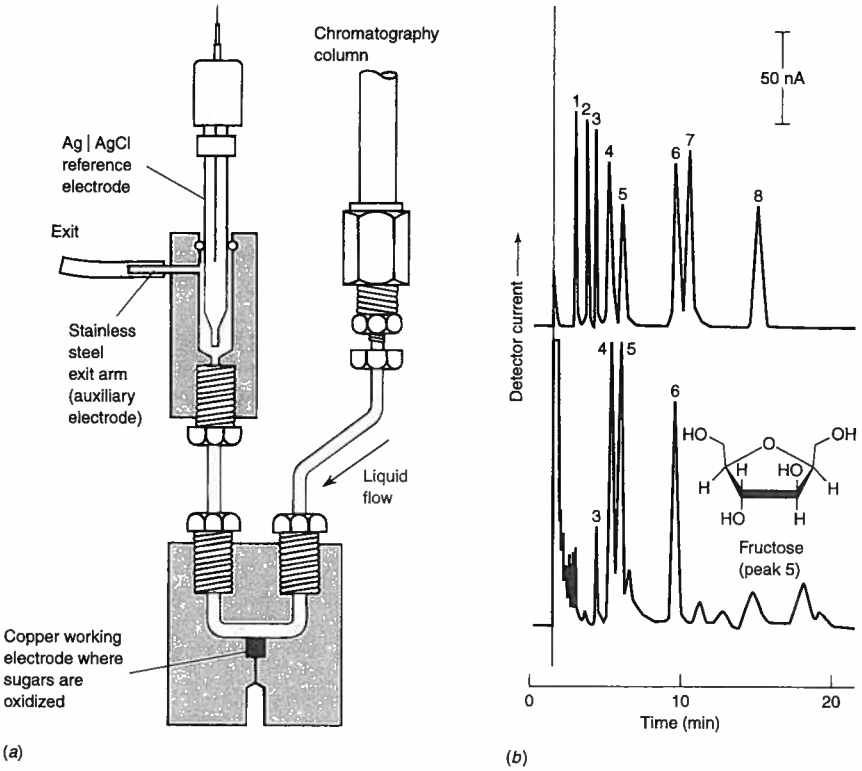
16 Electroanalytical Techniques

HOW SWEET IT IS!

(*a*) Electrochemical detector measures sugars emerging from a chromatography column. Sugars are oxidized at the Cu electrode, whose potential is regulated with respect to the Ag | AgCl reference electrode. Reduction ($H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$) occurs at the stainless steel exit arm, and electric current is measured between Cu and steel. [Adapted from Bioanalytical Systems, West Lafayette, IN.] (*b*) Anion-exchange separation of sugars in 0.1 M NaOH with CarboPac PA1 column. Upper chromatogram shows a standard mixture of (1) fucose, (2) methylglucose, (3) arabinose, (4) glucose, (5) fructose, (6) lactose, (7) sucrose, and (8) cellobiose. Lower chromatogram was obtained with Bud Dry beer diluted by a factor of 100 with water and filtered through a 0.45-μm membrane to remove particles. [From P. Luo, M. Z. Luo, and R. P. Baldwin, "Determination of Sugars in Food Products," *J. Chem. Ed.* 1993, *70*, 679.]



You can measure sugars in your favorite beverage by separating the sugars by anion-exchange chromatography (Chapter 25) in strongly basic solution and detecting them with an electrode as they emerge from the column.[1] The —OH groups of sugars such as fructose, whose structure is shown in the chromatogram, partially dissociate to $—O^-$ anions in 0.1 M NaOH. Anions are separated from one another when they pass through a column that has fixed positive charges. As sugars emerge from the column, they are detected by oxidation at a Cu electrode poised at a potential of +0.55 V versus Ag | AgCl. The chromatogram is a graph of detector current versus time. Each sugar gives a peak whose area is proportional to the moles exiting the column.

	Sugar concentration (g/L)			
Brand	**Glucose**	**Fructose**	**Lactose**	**Maltose**
Budweiser	0.54	0.26	0.84	2.05
Bud Dry	0.14	0.29	0.46	—
Coca-Cola	45.1	68.4	—	1.04
Pepsi	44.0	42.9	—	1.06
Diet Pepsi	0.03	0.01	—	—

Electrolytic production of aluminum by the Hall-Héroult process consumes ~5% of the electrical output of the United States! Al^{3+} in a molten solution of Al_2O_3 and cryolite (Na_3AlF_6) is reduced to Al at the cathode of a cell that typically draws 250 kA. This process was invented by Charles Hall in 1886 when he was 22 years old, just after graduating from Oberlin College.[2]

Charles Martin Hall. [Courtesy of Alcoa.]

Convention: *cathodic current* is considered *positive.*

Previous chapters dealt with *potentiometry*—in which voltage was measured in the absence of significant current. Now we consider electroanalytical methods in which current is essential.[3] Techniques in this chapter are all examples of **electrolysis**—the process in which a chemical reaction is forced to occur at an electrode by an imposed voltage (Demonstration 16-1). The home glucose monitor described in this chapter, with sales of more than $3 billion in 2007, is the single largest electroanalytical application.

16-1 Fundamentals of Electrolysis

Suppose we dip Cu and Pt electrodes into a solution of Cu^{2+} and force electric current through to deposit copper metal at the cathode and to liberate O_2 at the anode.

Cathode: $$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$$

Anode: $$H_2O \rightleftharpoons \frac{1}{2}O_2(g) + 2H^+ + 2e^-$$

Net reaction: $$H_2O + Cu^{2+} \rightleftharpoons Cu(s) + \frac{1}{2}O_2(g) + 2H^+ \qquad (16\text{-}1)$$

Figure 16-1 shows how we might conduct the experiment. The potentiometer measures the voltage applied by the power source. The ammeter measures the current flowing through the circuit.

The electrode at which the reaction of interest occurs is called the **working electrode.** In Figure 16-1, we happen to be interested in reduction of Cu^{2+}, so Cu is the working electrode. The other electrode is called the *counter electrode.* We adopt the convention that *current is positive if reduction occurs at the working electrode.*

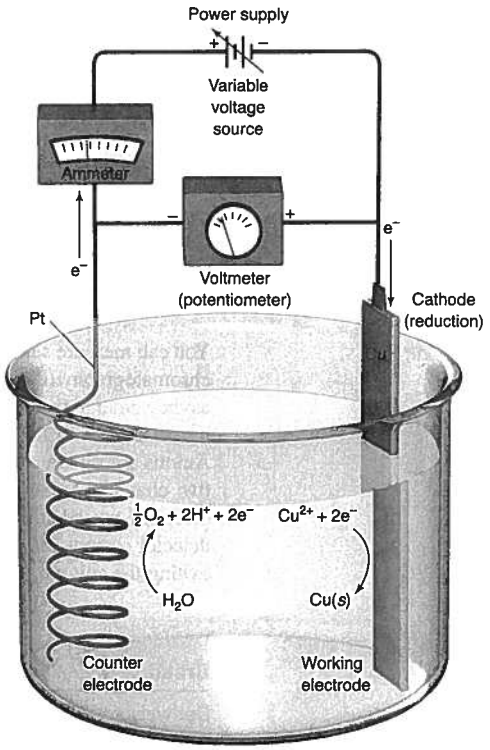


FIGURE 16-1 Electrolysis experiment. The power supply  is a variable voltage source. The potentiometer measures voltage and the ammeter measures current.

Current Measures the Rate of Reaction

If a current I flows for a time t, the charge q passing any point in the circuit is

Relation of charge to current and time: $$q = I \cdot t \qquad (16\text{-}2)$$

Coulombs Amperes · Seconds

An *ampere* is an electric current of 1 coulomb per second.

A *coulomb* contains $6.241\ 5 \times 10^{18}$ electrons.

The number of moles of electrons is

$$\text{Moles of } e^- = \frac{\text{coulombs}}{\text{coulombs/mole}} = \frac{I \cdot t}{F}.$$

Faraday constant: $F = 9.648\,5 \times 10^4$ C/mol

$$\text{moles of electrons} = \frac{I \cdot t}{F}$$

If a reaction requires n electrons per molecule, the quantity reacting in time t is

Relation of moles to current and time:

$$\text{Moles reacted} = \frac{I \cdot t}{nF} \qquad (16\text{-}3)$$

EXAMPLE **Relating Current, Time, and Amount of Reaction**

If a current of 0.17 A flows for 16 min through the cell in Figure 16-1, how many grams of Cu(s) will be deposited?

Solution We first calculate the moles of e^- flowing through the cell:

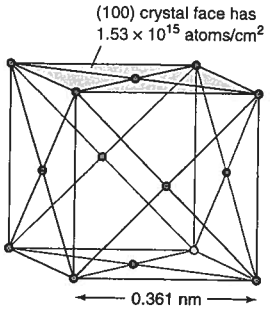
$$\text{Moles of } e^- = \frac{I \cdot t}{F} = \frac{\left(0.17 \frac{C}{s}\right)(16 \text{ min})\left(60 \frac{s}{\text{min}}\right)}{96\,485\left(\frac{C}{\text{mol}}\right)} = 1.6_9 \times 10^{-3} \text{ mol}$$

The cathode half-reaction requires $2e^-$ for each Cu deposited. Therefore,

$$\text{Moles of Cu}(s) = \frac{1}{2}(\text{moles of } e^-) = 8.4_5 \times 10^{-4} \text{ mol}$$

The mass of Cu(s) deposited is $(8.4_5 \times 10^{-4}$ mol)(63.546 g/mol) = 0.054 g.

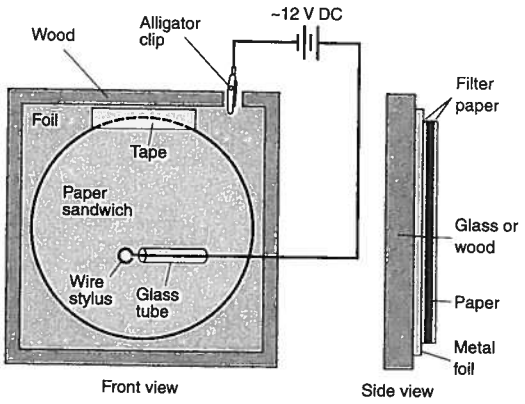
Test Yourself A *monolayer* (single layer of atoms) of Cu on the crystal face shown in the margin has 1.53×10^{15} atoms/cm^2 $= 2.54 \times 10^{-9}$ mol/cm^2. What current can deposit one layer of Cu atoms on 1 cm^2 in 1 s? (***Answer:*** 0.490 mA)



Face-centered cubic crystal

DEMONSTRATION 16-1 **Electrochemical Writing**[4]

Approximately 7% of electric power in the United States goes into electrolytic chemical production. The electrolysis apparatus pictured here consists of a sheet of Al foil taped or cemented to a wood surface. Any size will work, but an area of 15 cm on a side is convenient for a classroom demonstration. Tape to the metal foil (at one edge only) a sandwich consisting of filter paper, printer paper, and another sheet of filter paper. Make a stylus from Cu wire (18 gauge or thicker) looped at one end and passed through a length of glass tubing.



Prepare a fresh solution from 1.6 g of KI, 20 mL of water, 5 mL of 1 wt% starch solution, and 5 mL of phenolphthalein indicator solution. (If the solution darkens after several days, decolorize it with a few drops of dilute $Na_2S_2O_3$.) Soak the three layers of paper with the KI-starch-phenolphthalein solution. Connect the stylus and foil to a 12 V DC power source, and write on the paper with the stylus.

When the stylus is the cathode, water is reduced to H_2 plus OH^- and pink color appears from the reaction of OH^- with phenolphthalein.

$$\text{Cathode:} \quad H_2O + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-$$

When the polarity is reversed and the stylus is the anode, I^- is oxidized to I_2; a black (very dark blue) color appears from the reaction of I_2 with starch.

$$\text{Anode:} \quad I^- \rightarrow \frac{1}{2}I_2 + e^-$$

Pick up the top sheet of filter paper and the printer paper, and you will discover that the writing appears in the opposite color on the bottom sheet of filter paper (Color Plate 10).

Voltage Changes When Current Flows

Figure 16-1 is drawn with the same conventions as Figures 13-4 and 13-6. The cathode—where reduction occurs—is at the right side of the figure. The positive terminal of the potentiometer is on the right-hand side.

If electric current is negligible, the cell voltage is

$$E = E(\text{cathode}) - E(\text{anode}) \qquad \textbf{(16-4)}$$

To use $E = E(\text{cathode}) - E(\text{anode})$, you must write both reactions as *reductions*. $E(\text{cathode}) - E(\text{anode})$ is the *open-circuit* voltage. It is the voltage measured with negligible current flowing between cathode and anode.

The *cathode* is the electrode connected to the *negative* terminal of the power supply.

In Chapter 13, we wrote $E = E_+ - E_-$, where E_+ is the potential of the electrode attached to the positive terminal of the potentiometer and E_- is the potential of the electrode attached to the negative terminal of the potentiometer. Equation 16-4 is equivalent to $E = E_+ - E_-$. The polarity of the potentiometer in Figure 16-1 is the same as in Figures 13-4 and 13-6. In an electrolysis, electrons come from the negative terminal of the power supply into the cathode of the electrolysis cell. E(cathode) is the potential of the electrode connected to the negative terminal of the power supply, and E(anode) is the potential of the electrode connected to the positive terminal of the power supply.

If Reaction 16-1 contains 0.20 M Cu^{2+} and 1.0 M H^+ and liberates O_2 at a pressure of 1.0 bar, we find

$$E = \underbrace{\left\{0.339 - \frac{0.059\,16}{2}\log\left(\frac{1}{[Cu^{2+}]}\right)\right\}}_{E\text{ (cathode)}} - \underbrace{\left\{1.229 - \frac{0.059\,16}{2}\log\left(\frac{1}{P_{O_2}^{1/2}[H^+]^2}\right)\right\}}_{E\text{ (anode)}}$$

$$= \left\{0.339 - \frac{0.059\,16}{2}\log\left(\frac{1}{[0.20]}\right)\right\} - \left\{1.229 - \frac{0.059\,16}{2}\log\left(\frac{1}{(1.0)^{1/2}[1.0]^2}\right)\right\}$$

$$= 0.318 - 1.229 = -0.911\text{ V}$$

This voltage would be read on the potentiometer in Figure 16-1 if there were negligible current. The voltage is negative because the positive terminal of the potentiometer is connected to the negative side of the power supply. The free energy change computed in the margin is positive because the reaction is not spontaneous. We need the power supply to force the reaction to occur. If current is not negligible, *overpotential*, *ohmic potential*, and *concentration polarization* can change the voltage required to drive the reaction.

Free energy change for Reaction 16-1:

$$\Delta G = -nFE = -nF(-0.911\text{ V})$$
$$= -(2)\left(96\,485\,\frac{\text{C}}{\text{mol}}\right)(-0.911\text{ V})$$
$$= +1.76 \times 10^5\text{ C} \cdot \text{V/mol}$$
$$= +1.76 \times 10^5\text{ J/mol} = 176\text{ kJ/mol}$$

Note that C × V = J

Overpotential is the voltage required to overcome the *activation energy* for a reaction at an electrode (Figure 16-2).[5] The faster you wish to drive the reaction, the greater the overpotential that must be applied. Electric current measures the rate of electron transfer. Applying a greater overpotential will sustain a higher *current density* (current per unit area of electrode surface, A/m^2). Table 16-1 shows that the overpotential for liberation of H_2 at a Cu surface must be increased from 0.479 to 1.254 V to increase the current density from 10 A/m^2 to 10 000 A/m^2. Activation energy depends on the nature of the surface. H_2 is evolved at a Pt surface with little overpotential, whereas a Hg surface requires ~1 V to drive the reaction.

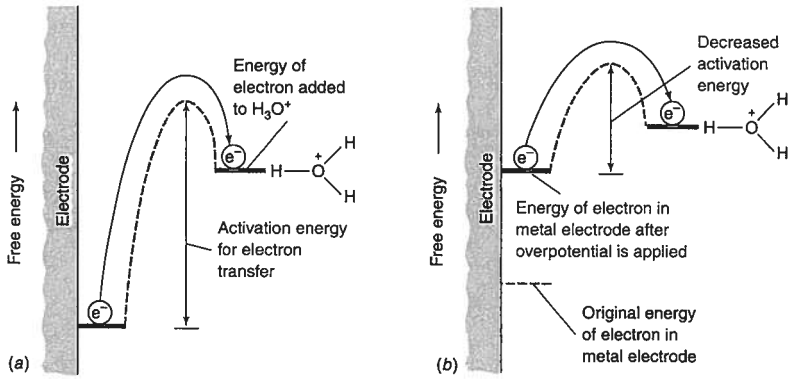


FIGURE 16-2 (*a*) Schematic energy profile for electron transfer from a metal to H_3O^+, leading to liberation of H_2. (*b*) Applying a potential to the metal raises the energy of the electron in the metal and decreases the activation energy for electron transfer.

Ohmic potential is the voltage needed to overcome electrical resistance, R, of the solution in the electrochemical cell when a current, I, is flowing:

Ohmic potential: $$E_{\text{ohmic}} = IR \qquad \textbf{(16-5)}$$

TABLE 16-1 Overpotential (V) for gas evolution at various current densities (A/m^2) at 25°C

	10 A/m^2		100 A/m^2		1 000 A/m^2		10 000 A/m^2	
Electrode	H_2	O_2	H_2	O_2	H_2	O_2	H_2	O_2
Platinized Pt	0.015 4	0.398	0.030 0	0.521	0.040 5	0.638	0.048 3	0.766
Smooth Pt	0.024	0.721	0.068	0.85	0.288	1.28	0.676	1.49
Cu	0.479	0.422	0.584	0.580	0.801	0.660	1.254	0.793
Ag	0.475 1	0.580	0.761 8	0.729	0.874 9	0.984	1.089 0	1.131
Au	0.241	0.673	0.390	0.963	0.588	1.244	0.798	1.63
Graphite	0.599 5		0.778 8		0.977 4		1.220 0	
Pb	0.52		1.090		1.179		1.262	
Zn	0.716		0.746		1.064		1.229	
Hg	0.9		1.0		1.1		1.1	

SOURCE: International Critical Tables, 1929, 6, 339. This reference also gives overpotentials for Cl_2, Br_2, and I_2.

If the cell has a resistance of 2 ohms and a current of 20 mA is flowing, the voltage required to overcome the resistance is $E = (2\ \Omega)(20\ \text{mA}) = 0.040\ \text{V}$.

Resistance is measured in ohms, whose symbol is capital Greek omega, Ω.

Concentration polarization occurs when the concentrations of reactants or products are not the same at the surface of the electrode as they are in bulk solution. For Reaction 16-1, the Nernst equation should be written

$$E(\text{cathode}) = 0.339 - \frac{0.059\ 16}{2}\log\left(\frac{1}{[Cu^{2+}]_s}\right)$$

Electrodes respond to concentrations of reactants and products adjacent to the electrode, not to concentrations in the bulk solution.

where $[Cu^{2+}]_s$ is the concentration in the solution *at the surface of the electrode*. If reduction of Cu^{2+} occurs rapidly, $[Cu^{2+}]_s$ could be very small because Cu^{2+} cannot diffuse to the electrode as fast as it is consumed. As $[Cu^{2+}]_s$ decreases, E(cathode) becomes more negative.

If $[Cu^{2+}]_s$ were reduced from 0.2 M to 2 μM, E(cathode) would change from 0.318 to 0.170 V.

Overpotential, ohmic potential, and concentration polarization make electrolysis more difficult. They drive the cell voltage more negative, requiring more voltage from the power supply in Figure 16-1 to drive the reaction forward.

$$E = \underbrace{E(\text{cathode}) - E(\text{anode})}_{\text{These terms include the effects of concentration polarization}} - IR - \text{overpotentials} \qquad \textbf{(16-6)}$$

There can be concentration polarization and overpotential at both the cathode and the anode.

EXAMPLE **Effects of Ohmic Potential, Overpotential, and Concentration Polarization**

Suppose we wish to electrolyze I^- to I_3^- in a 0.10 M KI solution containing 3.0×10^{-5} M I_3^- at pH 10.00 with P_{H_2} fixed at 1.00 bar.

$$3I^- + 2H_2O \rightarrow I_3^- + H_2(g) + 2OH^-$$

(a) Find the cell voltage if no current is flowing. **(b)** Then suppose that electrolysis increases $[I_3^-]_s$ to 3.0×10^{-4} M, but other concentrations are unaffected. Suppose that the cell resistance is 2.0 Ω, the current is 63 mA, the cathode overpotential is 0.382 V, and the anode overpotential is 0.025 V. What voltage is needed to drive the reaction?

Solution **(a)** The open-circuit voltage is E(cathode) − E(anode):

Cathode: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ $\quad E^\circ = -0.828\ \text{V}$

Anode: $I_3^- + 2e^- \rightarrow 3I^-$ $\quad E^\circ = 0.535\ \text{V}$

$$E(\text{cathode}) = -0.828 - \frac{0.059\ 16}{2}\log(P_{H_2}[OH^-]^2)$$

$$= -0.828 - \frac{0.059\ 16}{2}\log[(1.00)(1.0 \times 10^{-4})^2] = -0.591\ \text{V}$$

$$E(\text{anode}) = 0.535 - \frac{0.059\,16}{2}\log\left(\frac{[I^-]^3}{[I_3^-]}\right)$$

$$= 0.535 - \frac{0.059\,16}{2}\log\left(\frac{[0.10]^3}{[3.0 \times 10^{-5}]}\right) = 0.490 \text{ V}$$

$$E = E(\text{cathode}) - E(\text{anode}) = -1.081 \text{ V}$$

We would have to apply -1.081 V to force the reaction to occur.

(b) Now E(cathode) is unchanged but E(anode) changes because $[I_3^-]_s$ is different from $[I_3^-]$ in bulk solution.

$$E(\text{anode}) = 0.535 - \frac{0.059\,16}{2}\log\left(\frac{[0.10]^3}{[3.0 \times 10^{-4}]}\right) = 0.520 \text{ V}$$

$$E = E(\text{cathode}) - E(\text{anode}) - IR - \text{overpotentials}$$

$$= -0.591 \text{ V} - 0.520 \text{ V} - (2.0\ \Omega)(0.063 \text{ A}) - 0.382 \text{ V} - 0.025 \text{ V}$$

$$= -1.644 \text{ V}$$

Instead of -1.081 V, we need to apply -1.644 V to drive the reaction.

Test Yourself Find the voltage in part **(b)** if $[I^-]_s = 0.01$ M. (***Answer:*** -1.732 V)

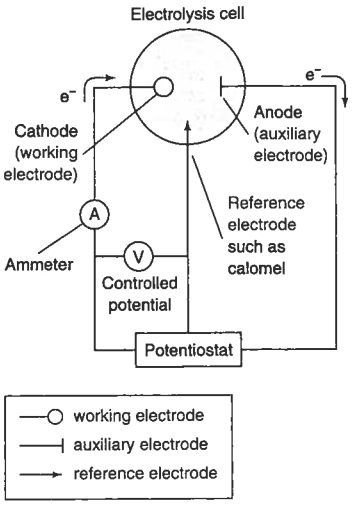


FIGURE 16-3 Circuit used for controlled-potential electrolysis with a three-electrode cell.

Working electrode: where the analytical reaction occurs

Auxiliary electrode: the other electrode needed for current flow

Reference electrode: used to measure the potential of the working electrode

The chromatographic detector at the opening of this chapter has a Cu working electrode, a stainless steel auxiliary electrode, and a Ag | AgCl reference electrode.

Controlled-Potential Electrolysis with a Three-Electrode Cell

An **electroactive species** is one that can be oxidized or reduced at an electrode. We regulate the potential of the working electrode to control which species react and which do not. Metal electrodes are said to be **polarizable,** which means that their potentials are easily changed when small currents flow. A reference electrode such as calomel or Ag | AgCl is said to be **nonpolarizable,** because its potential does not vary much unless a significant current is flowing. Ideally, we want to measure the potential of a polarizable working electrode with respect to a nonpolarizable reference electrode. How can we do this if there is to be significant current at the working electrode and negligible current at the reference electrode?

The answer is to introduce a third electrode (Figure 16-3). The **working electrode** is the one at which the reaction of interest occurs. A calomel or other **reference electrode** is used to measure the potential of the working electrode. The **auxiliary electrode** (also called the *counter electrode*) is the current-supporting partner of the working electrode. Current flows between the working and the auxiliary electrodes. Negligible current flows through the reference electrode, so its potential is unaffected by ohmic potential, concentration polarization, and overpotential. It truly maintains a constant reference potential. In **controlled-potential electrolysis,** the voltage difference between the working and reference electrodes in a three-electrode cell is regulated by an electronic device called a **potentiostat.**

Concentration polarization and overpotential can both occur at the working and auxiliary electrodes. There is an ohmic potential drop between the working and auxiliary electrodes. To obtain the best measurement of the working electrode potential, the reference electrode should be placed as close as possible to the working electrode (Figure 16-4).

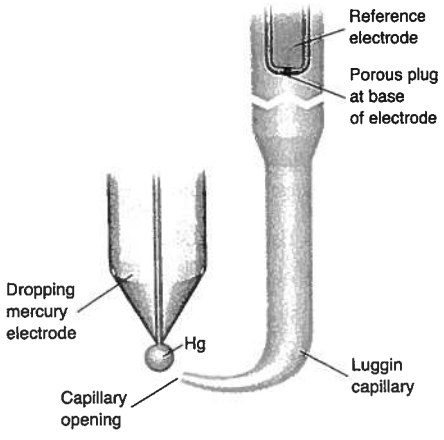


FIGURE 16-4 Use of a Luggin capillary to position a reference electrode as close as possible to the working electrode (shown as a dropping mercury electrode in this illustration). The capillary, with an opening of ~0.2 mm, is filled with the same electrolyte that is in the analyte solution. The reference electrode is in contact with the capillary solution. There is negligible current in the capillary, so there is negligible ohmic loss between the tip of the capillary and the reference electrode.

16-2 Electrogravimetric Analysis

In **electrogravimetric analysis,** analyte is quantitatively deposited on an electrode by electrolysis. The electrode is weighed before and after deposition. The increase in mass tells us how much analyte was deposited. We can measure Cu^{2+} in a solution by reducing it to Cu(s) on a clean Pt gauze cathode with a large surface area (Figure 16-5). O_2 is liberated at the counter electrode.

How do you know when electrolysis is complete? One way is to observe the disappearance of color in a solution from which a colored species such as Cu^{2+} or Co^{2+} is removed. Another way is to expose most, but not all, of the surface of the cathode to the solution during electrolysis. To test whether or not the reaction is complete, raise the beaker or add water so that fresh surface of the cathode is exposed to the solution. After an additional period of electrolysis (15 min, say), see if the newly exposed electrode surface has a deposit. If it does, repeat the procedure. If not, the electrolysis is done. A third method is to remove a drop of solution and perform a qualitative test for analyte.

Tests for completion of the deposition:

- disappearance of color
- no deposition on freshly exposed electrode surface
- qualitative test for analyte in solution

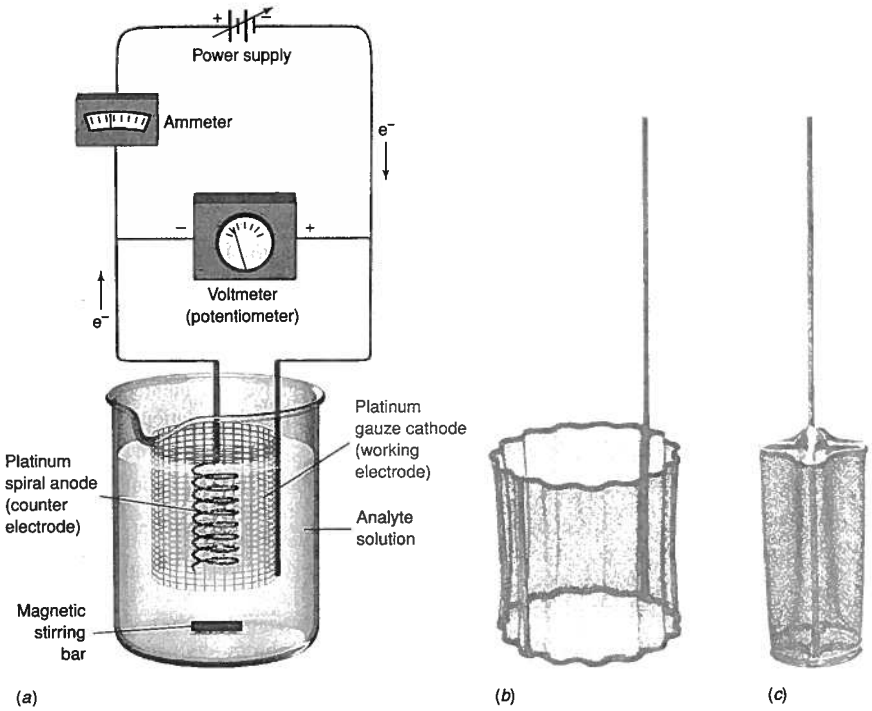


FIGURE 16-5 (*a*) Electrogravimetric analysis. Analyte is deposited on the large Pt gauze electrode. If analyte is to be oxidized, rather than reduced, the polarity of the power supply is reversed so that deposition still occurs on the large electrode. (*b*) Outer Pt gauze electrode. (*c*) Optional inner Pt gauze electrode designed to be spun by a motor in place of magnetic stirring.

In the preceding section, we calculated that −0.911 V needs to be applied between the electrodes to deposit Cu(s) on the cathode. The actual behavior of the electrolysis in Figure 16-6 shows that nothing special happens at −0.911 V. Near −2 V, the reaction begins in earnest. At low voltage, a small *residual current* is observed from reduction at the cathode and an equal amount of oxidation at the anode. Reduction might involve traces of dissolved O_2, impurities such as Fe^{3+}, or surface oxide on the electrode.

Table 16-1 shows that an overpotential of ~1 V is required for O_2 formation at the smooth Pt anode. Overpotential is the main reason why not much happens in Figure 16-6 until −2 V is applied. Beyond −2 V, the rate of reaction (the current) increases steadily. Around −4.6 V, the current increases more rapidly with the onset of reduction of H_3O^+ to H_2. Gas bubbles at the working electrode interfere with deposition of solids.

The voltage between the two electrodes is

$$E = E(\text{cathode}) - E(\text{anode}) - IR - \text{overpotentials} \qquad (16\text{-}6)$$

Suppose we hold the applied potential at $E = -2.0$ V. As Cu^{2+} is used up, the current decreases and both ohmic and overpotentials decrease in magnitude. E(anode) is fairly

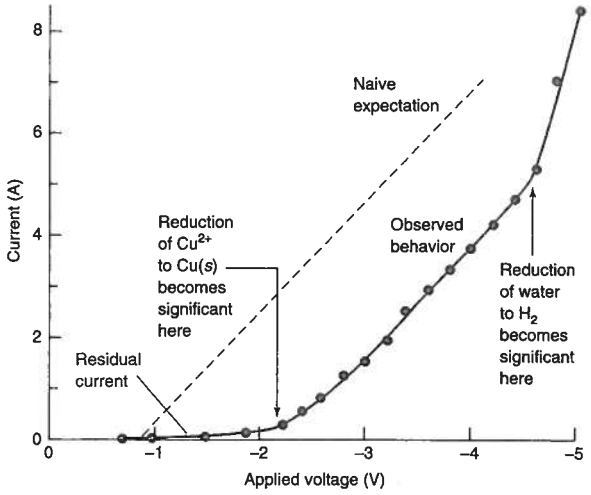


FIGURE 16-6 Observed current-voltage relation for electrolysis of 0.2 M $CuSO_4$ in 1 M $HClO_4$ under N_2, using the apparatus in Figure 16-5.

constant because of the high concentration of solvent being oxidized at the anode ($H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$). If E and E(anode) are constant and if IR and overpotentials decrease in magnitude, then *E(cathode) must become more negative* to maintain the algebraic equality in Equation 16-6. E(cathode) drops in Figure 16-7 to -0.4 V, at which H_3O^+ is reduced to H_2. As E(cathode) falls from $+0.3$ V to -0.4 V, other ions such as Co^{2+}, Sn^{2+}, and Ni^{2+} can be reduced. In general, then, *when the applied voltage is constant, the cathode potential drifts to more negative values and other solutes might be reduced.*

A *cathodic depolarizer* is reduced in preference to solvent. For *oxidation* reactions, *anodic depolarizers* include N_2H_4 (hydrazine) and NH_2OH (hydroxylamine).

To prevent the cathode potential from becoming so negative that unintended ions are reduced, a cathodic **depolarizer** such as NO_3^- can be added to the solution. The cathodic depolarizer is more easily reduced than H_3O^+:

$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$$

Alternatively, we can use a three-electrode cell (Figure 16-3) with a potentiostat to control the cathode potential and prevent unwanted side reactions.

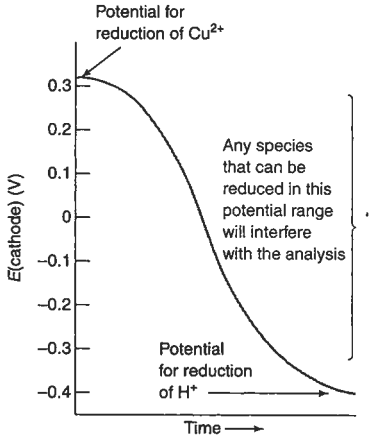


FIGURE 16-7 E(cathode) becomes more negative with time when electrolysis is conducted in a two-electrode cell with a constant voltage between the electrodes.

EXAMPLE **Controlled-Potential Electrolysis**

What cathode potential is required to reduce 99.99% of 0.10 M Cu^{2+} to Cu(s)? Is it possible to remove this Cu^{2+} without reducing 0.10 M Sn^{2+} in the same solution?

$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ = 0.339 \text{ V} \tag{16-7}$$

$$Sn^{2+} + 2e^- \rightleftharpoons Sn(s) \qquad E^\circ = -0.141 \text{ V} \tag{16-8}$$

Solution If 99.99% of Cu^{2+} were reduced, the concentration of remaining Cu^{2+} would be 1.0×10^{-5} M, and the required cathode potential would be

$$E(\text{cathode}) = 0.339 - \frac{0.059\,16}{2}\log\left(\frac{1}{\underbrace{1.0 \times 10^{-5}}_{[Cu^{2+}]}}\right) = 0.19 \text{ V}$$

The cathode potential required to reduce Sn^{2+} is

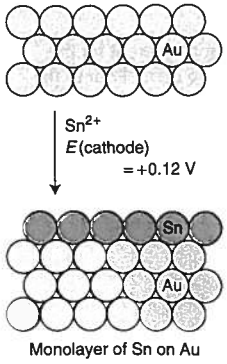
$$E(\text{cathode, for reduction of } Sn^{2+}) = -0.141 - \frac{0.059\,16}{2}\log\left(\frac{1}{\underbrace{0.10}_{[Sn^{2+}]}}\right) = -0.17 \text{ V}$$

We do not expect reduction of Sn^{2+} at a cathode potential more positive than -0.17 V. The reduction of 99.99% of Cu^{2+} without reducing Sn^{2+} appears feasible.

Test Yourself Will E(cathode) = 0.19 V reduce 0.10 M SbO^+ at pH 2 by the reaction $SbO^+ + 2H^+ + 3e^- \rightleftharpoons Sb(s) + H_2O$, $E^\circ = 0.208$ V? (***Answer:*** E(cathode) for SbO^+ = 0.11 V, so reduction should not occur at 0.19 V)

Underpotential Deposition

When Sn^{2+} in 1 M HCl is electrolyzed at a gold working electrode, reduction is observed at E(cathode) = −0.18 V by the technique of cyclic voltammetry, which we study later in this chapter. From what you know so far, you should not expect that potentials more positive than −0.18 V will reduce Sn^{2+}. Yet, a small current is observed at E(cathode) = +0.12 V. The coulombs required at −0.18 V increase in proportion to $[Sn^{2+}]$. The coulombs required at +0.12 V are just enough to produce 8.7×10^{-10} mol Sn(s) per square centimeter of gold electrode surface.[6] Then no more current flows at E(cathode) = +0.12 V.



Monolayer of Sn on Au

Reduction at +0.12 V is called **underpotential deposition.** It occurs at a potential that is not predicted to reduce Sn^{2+} to bulk Sn(s). It is explained by the reaction

$$Sn^{2+} + 2e^- \rightleftharpoons Sn(\textit{monolayer on Au}) \qquad \textbf{(16-9)}$$

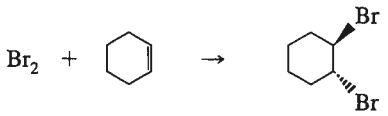
in which the product is a one-atom-thick layer of tin on gold. It is thermodynamically more favorable to deposit a layer of tin atoms on gold than it is to deposit a fresh layer of tin on bulk tin metal. Therefore, the potential for Reaction 16-9 is more positive than the potential for Reaction 16-8.

16-3 Coulometry

Coulometry is a chemical analysis based on counting the electrons used in a reaction. For example, cyclohexene can be titrated with Br_2 generated by electrolytic oxidation of Br^-:

Coulometric methods are based on measuring the number of electrons that participate in a chemical reaction.

$$2Br^- \rightarrow Br_2 + 2e^- \qquad \textbf{(16-10)}$$



Cyclohexene *trans*-1,2-Dibromocyclohexane

(16-11)

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br^-. When Reaction 16-10 has generated just enough Br_2 to react with all the cyclohexene, the moles of electrons liberated in Reaction 16-10 are equal to twice the moles of Br_2 and therefore twice the moles of cyclohexene.

The reaction is carried out *at a constant current* with the apparatus in Figure 16-8. Br_2 generated at the Pt anode at the left reacts with cyclohexene. When cyclohexene is consumed, the concentration of Br_2 suddenly rises, signaling the end of the reaction.

The rise in Br_2 concentration is detected by measuring the current between the two detector electrodes at the right in Figure 16-8. A voltage of 0.25 V applied between these two electrodes is not enough to electrolyze any solute, so only a tiny current of <1 μA flows through

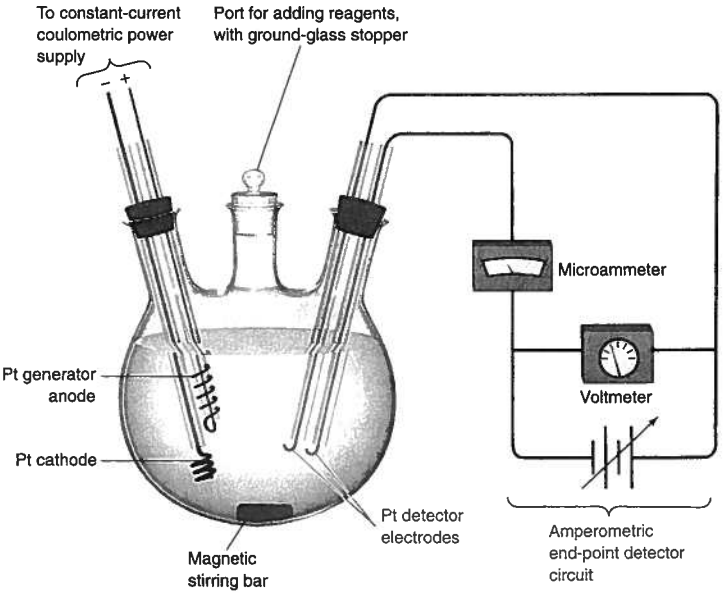


FIGURE 16-8 Apparatus for coulometric titration of cyclohexene with Br_2. The solution contains cyclohexene, 0.15 M KBr, and 3 mM mercuric acetate in a mixed solvent of acetic acid, methanol, and water. Mercuric acetate catalyzes the addition of Br_2 to the olefin. [Adapted from D. H. Evans, "Coulometric Titration of Cyclohexene with Bromine," *J. Chem. Ed.* 1968, *45*, 88.]

the microammeter. At the equivalence point, cyclohexene is consumed, $[Br_2]$ suddenly increases, and detector current flows by virtue of the reactions:

Both Br_2 and Br^- must be present for the detector half-reactions to occur. Prior to the equivalence point, there is Br^-, but virtually no Br_2.

$$\text{Detector anode:} \quad 2Br^- \rightarrow Br_2 + 2e^-$$
$$\text{Detector cathode:} \quad Br_2 + 2e^- \rightarrow 2Br^-$$

In practice, enough Br_2 is first generated in the absence of cyclohexene to give a detector current of 20.0 μA. When cyclohexene is added, the current decreases to a tiny value because Br_2 is consumed. Br_2 is then generated by the coulometric circuit, and the end point is taken when the detector again reaches 20.0 μA. Because the reaction is begun with Br_2 present, impurities that can react with Br_2 before analyte is added are eliminated.

The electrolysis current (not to be confused with the detector current) for the Br_2-generating electrodes is controlled by a hand-operated switch. As the detector current approaches 20.0 μA, you close the switch for shorter and shorter intervals. This practice is analogous to adding titrant dropwise from a buret near the end of a titration. The switch in the coulometer circuit serves as a "stopcock" for addition of Br_2 to the reaction. Modern instruments automate the entire procedure.

EXAMPLE **Coulometric Titration**

A 2.000-mL volume containing 0.611 3 mg of cyclohexene/mL is to be titrated in Figure 16-8. How much time is required for titration at a constant current of 4.825 mA?

Solution The moles of cyclohexene are

$$\frac{(2.000\ \text{mL})(0.611\ 3\ \text{mg/mL})}{(82.146\ \text{mg/mmol})} = 0.014\ 88\ \text{mmol}$$

In Reactions 16-10 and 16-11, each mole of cyclohexene requires 1 mol of Br_2, which requires 2 mol of electrons. For 0.014 88 mmol of cyclohexene to react, 0.029 76 mmol of electrons must flow. From Equation 16-3,

$$\text{Moles of } e^- = \frac{I \cdot t}{F} \Rightarrow t = \frac{(\text{moles of } e^-)F}{I}$$

$$t = \frac{(0.029\ 76 \times 10^{-3}\text{mol})(96\ 485\ \text{C/mol})}{(4.825 \times 10^{-3}\ \text{C/s})} = 595.1\ \text{s}$$

It will require just under 10 min to complete the reaction.

Test Yourself How much time is required to titrate 1.000 mg of cyclohexene at 4.000 mA? (***Answer:*** 587.3 s)

Advantages of coulometry:

- precision
- sensitivity
- generation of unstable reagents in situ

The Latin *in situ* means "in place." Reagent is used right where it is generated.

Commercial coulometers deliver electrons with an accuracy of ~0.1%. With extreme care, the Faraday constant has been measured to within several parts per million by coulometry.[7] Automated coulometers commonly generate H^+, OH^-, Ag^+, and I_2 to titrate analytes including CO_2, sulfites in food, and sulfide in wastewater.[8] Unstable reagents such as Ag^{2+}, Cu^+, Mn^{3+}, and Ti^{3+} can be generated and used in situ.

In Figure 16-8, the reactive species (Br_2) is generated at the anode. The cathode products (H_2 from solvent and Hg from the catalyst) do not interfere with the reaction of Br_2 and cyclohexene. In some cases, however, H_2 or Hg could react with analyte. Then it is desirable to separate the counter electrode from the analyte, using the cell in Figure 16-9. H_2 bubbles innocuously out of the cathode chamber without mixing with the bulk solution.

Types of Coulometry

Coulometry employs either a *constant current* or a *controlled potential*. Constant-current methods, like the preceding Br_2/cyclohexene example, are called **coulometric titrations.** If we know the current and the time of reaction, we know how many coulombs have been delivered from Equation 16-2: $q = I \cdot t$.

Controlled-potential coulometry in a three-electrode cell is more selective than constant-current coulometry. Because the working electrode potential is constant, current decreases exponentially as analyte concentration decreases. Charge is measured by integrating current over the time of the reaction:

The number of coulombs is equal to the area under a curve of current versus time. Problem 16-21 provides an example.

$$q = \int_0^t I\,dt \qquad \textbf{(16-12)}$$

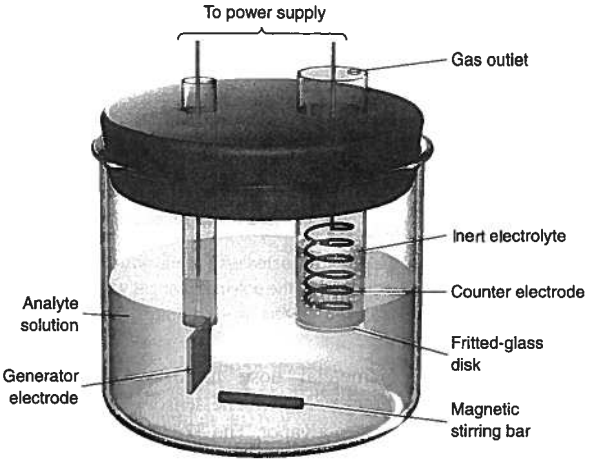


FIGURE 16-9 Isolating the counter electrode from analyte. Ions can flow through the porous fritted-glass disk. The liquid level in the counter electrode compartment should be higher than the liquid in the reactor so that analyte solution does not flow into the compartment.

In controlled-potential coulometry, current decays exponentially. You can approach the equivalence point by letting the current decay to a set value. For example, the current (*above* the residual current) will ideally be 0.1% of its initial value when 99.9% of the analyte has been consumed. Alternatively, the current versus time curve can be extrapolated according to its theoretical behavior after measuring its actual behavior for some time.

16-4 Amperometry

Amperometry: Electric current is proportional to the concentration of analyte.

Coulometry: Total number of electrons used for a reaction tells us how much analyte is present.

In **amperometry,** we measure the electric current between a pair of electrodes that are driving an electrolysis reaction. One reactant is the intended analyte, and the measured current is proportional to the concentration of analyte. The measurement of dissolved O_2 with the **Clark electrode** in Box 16-1 is based on amperometry. A different kind of sensor based on conductivity—the "electronic nose"—is described in Box 16-2.

Box 16-1 Clark Oxygen Electrode

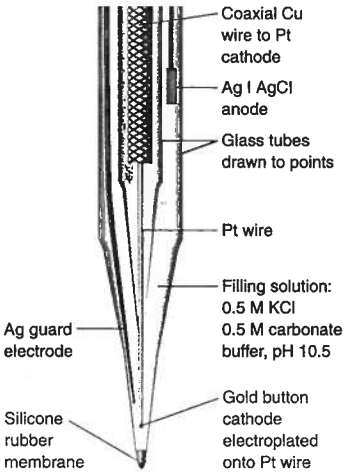
The Clark oxygen electrode[9] is widely used in medicine and biology to measure dissolved oxygen by amperometry. Leland Clark, who invented the electrode, also invented the glucose monitor and the heart-lung machine.

The glass body of the microelectrode in the figure is drawn to a fine point with a 5-μm opening at the base. Inside the opening is a 10- to 40-μm-long plug of silicone rubber, which is permeable to O_2. Oxygen diffuses into the electrode through the rubber and is reduced at the Au tip on the Pt wire, which is held at −0.75 V with respect to the Ag | AgCl reference electrode:

Pt | Au cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Ag | AgCl anode: $4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-$

A Clark electrode is calibrated by placing it in solutions of known O_2 concentration, and a graph of current versus $[O_2]$ is constructed. The electrode also contains a silver *guard electrode* extending most of the way to the bottom. The guard electrode is kept at a negative potential so that any O_2 diffusing in from the top of the electrode is reduced and does not interfere with measurement of O_2 diffusing in through the silicone membrane at the bottom. Similar electrodes have been designed for detection of NO, H_2S, and CO.[10]

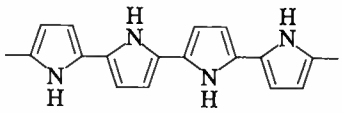


Clark oxygen microelectrode used to measure dissolved O_2 in small volumes. The tip of the cathode is plated with Au, which is less prone than Pt to fouling by adsorption of species from the test solution. [Adapted from N. P. Revsbech, "An Oxygen Microsensor with a Guard Column," *Limnol. Oceanogr.* 1989, *34*, 474.]

Box 16-2 What Is An "Electronic Nose"?

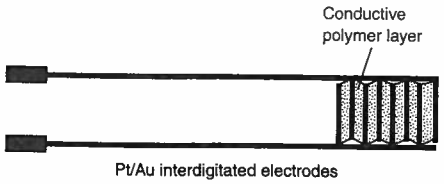
In the "old days," chemists prided themselves on their ability to identify compounds by odor. Smelling unknown chemicals is a bad idea because some vapors are toxic. Chemists are developing "electronic noses" that recognize odors to assess the freshness of meat, to find out if fruit is internally bruised, and to detect adulteration of food products.[11]

One approach to recognizing vapors is to coat interdigitated electrodes with an electronically conductive polymer, such as a derivative of polypyrrole.



Polypyrrole

When gaseous odor molecules are absorbed by the polymer, the electrical conductivity of the polymer changes. Different gases affect conductivity in different ways. Other sensor coatings are polymers containing conductive particles of silver or graphite. When the polymer absorbs small molecules, it swells and the conductivity decreases.



Interdigitated electrodes coated with conductive polymer to create an electronic nose. The conductivity of the polymer changes when it absorbs odor molecules. The spacing between "fingers" is ~0.25 mm.

One commercial "nose" has 32 sets of electrodes, each coated with a different polymer. The sensor yields 32 different responses when exposed to a vapor. The 32 changes are a "fingerprint" of the vapor. The electronic nose must be "trained" by pattern recognition algorithms to recognize an odor by its characteristic fingerprint. Other electronic noses are based on changes in optical absorption of polymers at the tips of optical fibers and on changes at the gates of field effect transistors (Section 14-8).

Enzyme: A protein that catalyzes a biochemical reaction. The enzyme increases the rate of reaction by many orders of magnitude.

Antibody: A protein that binds to a specific target molecule called an *antigen*. Antibodies bind to foreign cells that infect your body to initiate their destruction or identify them for attack by immune system cells.

Biosensors[12,13] use biological components such as *enzymes*, *antibodies*, or DNA for a highly selective response to one analyte. Biosensors that generate electric or optical signals are most common. Examples of amperometric biosensors are those that measure perchlorate in groundwater,[14] adenosine triphosphate (ATP) in biological tissue,[15] attomolar levels of genes,[16] and antibodies at femtomolar levels.[17] We now describe blood glucose monitors, which are, by far, the most widely used biosensors.

Blood Glucose Monitor

Diabetes afflicts approximately 5% of the population. Many people with diabetes must monitor their blood sugar (glucose) several times a day to control their disease through diet and insulin injections. Figure 16-10 shows a home glucose monitor featuring a disposable test strip with two carbon working electrodes and a Ag | AgCl reference electrode. As little as 4 μL of blood applied in the circular opening at the right of the figure is wicked over all three electrodes by a thin *hydrophilic* ("water loving") mesh. A 20-s measurement begins when the liquid reaches the reference electrode.

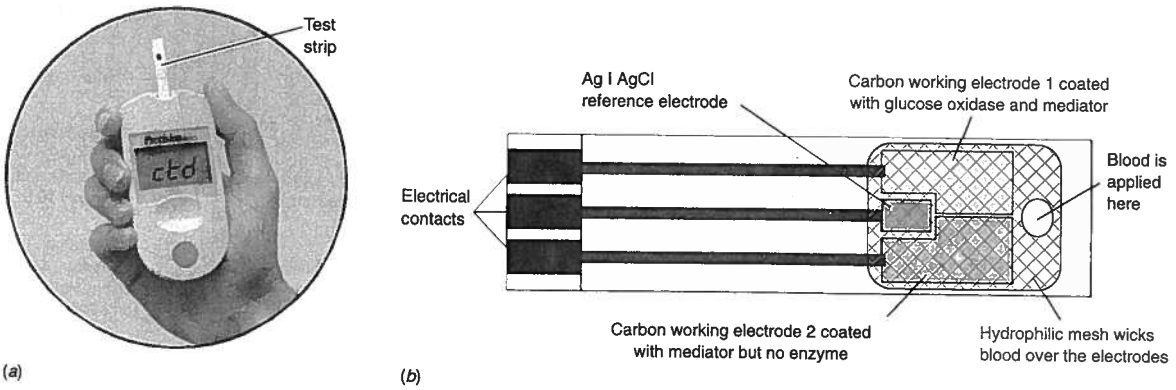
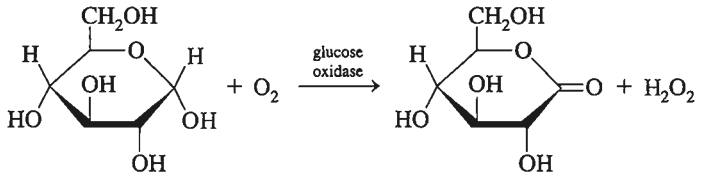


FIGURE 16-10 (*a*) Personal glucose monitor used by diabetics to measure blood sugar level. (*b*) Details of disposable test strip to which a drop of blood is applied. [Courtesy Abbott Laboratories MediSense Products, Bedford, MA.]

Working electrode 1 is coated with the enzyme *glucose oxidase* and a *mediator*, which we describe soon. The enzyme catalyzes the reaction of glucose with O_2:

Reaction in coating above working electrode 1:



Glucose — Oxygen — Gluconolactone — Hydrogen peroxide

(16-13)

In the absence of enzyme, the oxidation of glucose is negligible.

Early glucose monitors measured H_2O_2 from Reaction 16-13 by oxidation at a single working electrode, which was held at +0.6 V versus Ag | AgCl:

Reaction at working electrode 1:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad \textbf{(16-14)}$$

The current is proportional to the concentration of H_2O_2, which, in turn, is proportional to the glucose concentration in blood (Figure 16-11).

One problem with early glucose monitors is that their response depended on the concentration of O_2 in the enzyme layer, because O_2 participates in Reaction 16-13. If the O_2 concentration is low, the monitor responds as though the glucose concentration were low.

A good way to reduce O_2 dependence is to incorporate into the enzyme layer a species that substitutes for O_2 in Reaction 16-13. A substance that transports electrons between the analyte (glucose, in this case) and the electrode is called a **mediator.**

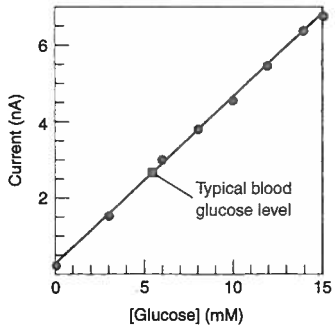
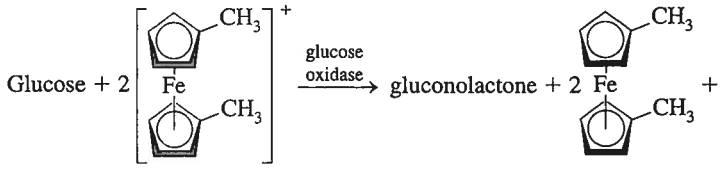


FIGURE 16-11 Response of an amperometric glucose electrode with dissolved O_2 concentration corresponding to an oxygen pressure of 0.027 bar, which is 20% lower than the typical concentration in subcutaneous tissue. [Data from S.-K. Jung and G. W. Wilson, "Polymeric Mercaptosilane-Modified Platinum Electrodes for Elimination of Interferents in Glucose Biosensors," *Anal. Chem.* 1996, *68*, 591.]

A *mediator* transports electrons between the analyte and the working electrode. The mediator undergoes no net reaction itself.

Reaction in coating above working electrode 1:



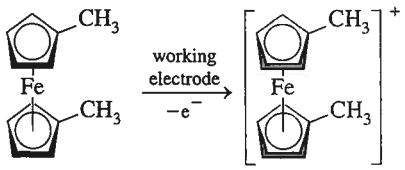
1,1'-Dimethylferricinium cation Mediator — 1,1'-Dimethylferrocene

(16-15)

Ferrocene contains flat, five-membered rings, similar to benzene. Each ring formally carries one negative charge, so the oxidation state of Fe, which sits between the rings, is +2. This molecule is called a *sandwich complex.*

The mediator consumed in Reaction 16-15 is then regenerated at the working electrode:

Reaction at working electrode 1:



(16-16)

The mediator lowers the required working electrode potential from 0.6 V to 0.2 V versus Ag | AgCl, thereby improving the stability of the sensor and eliminating some interference by other species in the blood.

The current at the working electrode is proportional to the concentration of ferrocene, which, in turn, is proportional to the concentration of glucose in the blood.

One problem with glucose monitors is that species such as ascorbic acid (vitamin C), uric acid, and acetaminophen (Tylenol) found in blood can be oxidized at the same potential required to oxidize the mediator in Reaction 16-16. To correct for this interference, the test strip in Figure 16-10 has a second indicator electrode coated with mediator, *but not with glucose oxidase*. Interfering species that are reduced at electrode 1 are also reduced at electrode 2. The current due to glucose is the current at electrode 1 *minus* the current at electrode 2 (both measured with respect to the reference electrode). Now you see why the test strip has two working electrodes.

A modified sensor measures glucose at a concentration of 2 fM in a 30-μL volume containing just 36 000 molecules of glucose.[18]

A challenge is to manufacture glucose monitors in such a reproducible manner that they do not require calibration. A user expects to add a drop of blood to the test strip and get a reliable reading without first constructing a calibration curve from known concentrations of glucose in blood. Each lot of test strips is highly reproducible and calibrated at the factory.

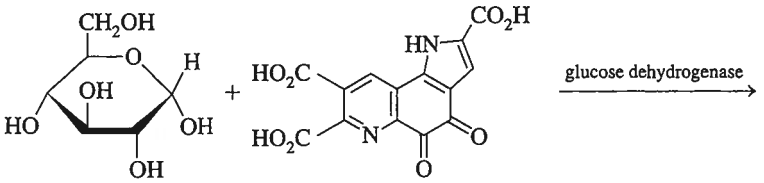
"Electrical Wiring" of Enzymes and Mediators for Blood Glucose Monitor

Demand for glucose monitors provides an economic stimulus for research that continues to improve the performance of home glucose monitors.[19] Noteworthy advances include (1) monitoring the reaction by coulometry instead of amperometry, (2) using a different enzyme to catalyze glucose oxidation, and (3) "electrical wiring" to increase the rate of reaction and to prevent reactants from diffusing away from the working electrode.

In *amperometry*, current flowing during glucose oxidation is measured. In *coulometry*, the number of electrons required to oxidize the glucose in a blood sample is counted. Amperometry measures the *rate of oxidation*. Coulometry measures the *number of molecules that have been oxidized*. The rate of reaction, and therefore the current, depends on temperature, but total charge transferred during oxidation is independent of temperature. Therefore, the coulometric measurement is independent of temperature. Total charge transferred is also insensitive to the activity of the enzyme (how quickly it works) and the mobility of the mediator, both of which affect current. Current is also affected by depletion of glucose during the measurement. In coulometry, the goal is to use up all the glucose.

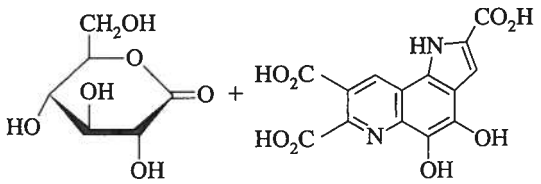
A *cofactor* is a small, nonprotein molecule that is bound to an enzyme and is necessary for the activity of the enzyme.

Replacing the enzyme glucose oxidase with *glucose dehydrogenase* eliminates O_2 as a reactant. A *cofactor* called PQQ, which is bound to glucose dehydrogenase, receives $2H^+ + 2e^-$ during the oxidation.



Glucose

Pyrroloquinoline quinone (PQQ) cofactor in glucose dehydrogenase



Gluconolactone $PQQH_2$ **(16-17)**

Unlike Reaction 16-13, O_2 is not involved in Reaction 16-17. Therefore, there is no dependence of the response to dissolved O_2.

In an "electrically wired" polymer gel on the surface of a carbon electrode (Figure 16-12), the enzyme and an osmium mediator are tethered to a polymer backbone. The $PQQH_2$ product of Reaction 16-17 is oxidized back to $PQQ + 2H^+$ by a nearby Os^{3+}. Os^{3+} is reduced to Os^{2+} in the process. Os^{2+} can exchange an electron with another Os^{3+}. Electrons are transported rapidly from Os to Os until they reach a carbon anode. Electrons then flow through a circuit to the Ag | AgCl counter electrode where AgCl is reduced to $Ag + Cl^-$.

"Electrical wiring" of the enzyme and the osmium mediators increases the current by a factor of 10 to 100 compared with an enzyme/mediator layer deposited onto an electrode. Increased current provides larger signal and a faster measurement. Covalent attachment of osmium to the polymer prevents the mediator from diffusing to the counter electrode, where it would react and create a large background current. Ligands for osmium are chosen so that the mildest possible potential (+0.1 V versus Ag | AgCl) can be applied to the electrode to oxidize glucose. At this potential, common oxidizable interferents produce acceptably small errors in glucose measurement.

The newest glucose monitor test strips require only 0.3 μL of blood for a measurement, significantly reducing the pain experienced by people who need to measure their glucose several times each day. Glucose in the entire volume is oxidized in about 1 min, and current is measured as a function of time. Integrating current versus time (Equation 16-12) gives the total charge required to reduce glucose.

Rotating Disk Electrode

A molecule has three ways to reach the surface of an electrode: (1) *diffusion* through a concentration gradient; (2) *convection*, which is the movement of bulk fluid by physical means

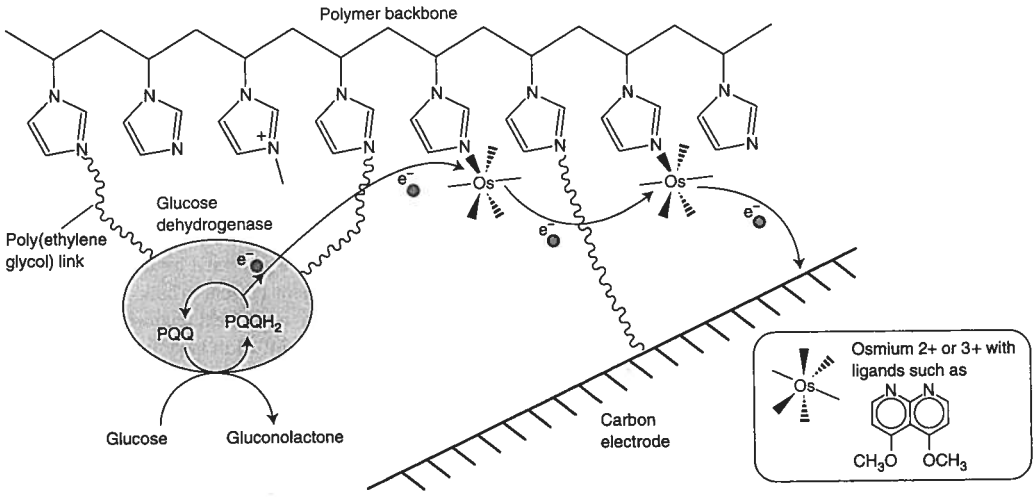


FIGURE 16-12 "Electrically wired" glucose dehydrogenase. The enzyme catalyzes the oxidation of glucose, reducing PQQ to $PQQH_2$. $PQQH_2$ is oxidized back to PQQ + $2H^+$ by Os^{3+}. Electrons move through successive osmium atoms until they reach the carbon anode. All members of the redox chain are bound to a polymer backbone.

such a stirring or boiling; and (3) *migration*, which is the attraction or repulsion of an ion by a charged surface. A common working electrode for amperometry is the **rotating disk electrode,** for which convection and diffusion control the flux of analyte to the electrode.[20]

When the electrode in Figure 16-13a is spun at ~1 000 revolutions per minute, a vortex is established that brings analyte near the electrode rapidly by convection. If the potential is great enough, analyte reacts rapidly at the electrode, thereby reducing the concentration of analyte at the surface to near 0. The resulting concentration gradient is shown schematically in Figure 16-13b. Analyte must traverse the final, short distance (~10–100 μm) by diffusion alone.

Three ways for analyte to reach an electrode:

- diffusion
- convection
- migration

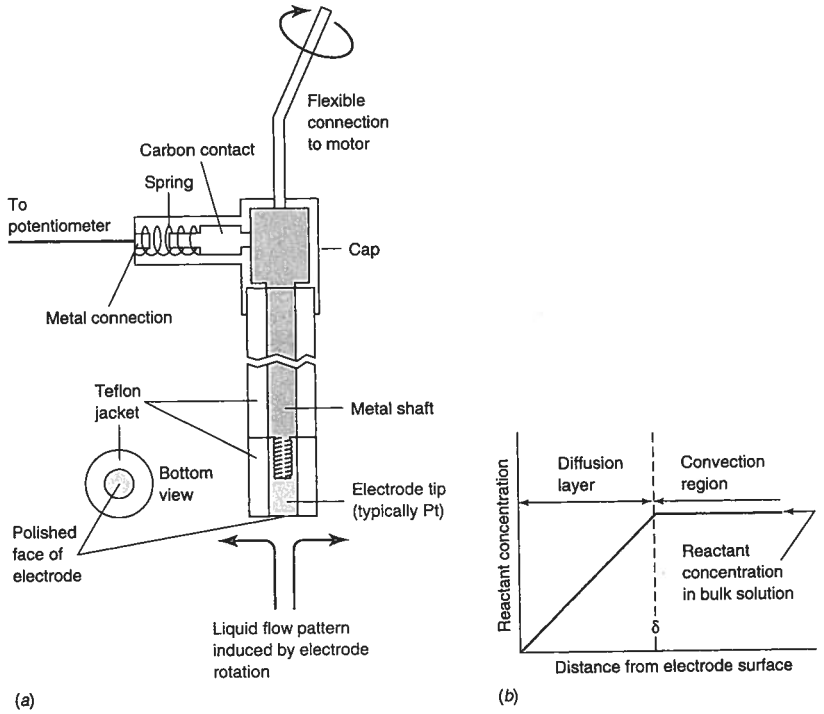


FIGURE 16-13 (*a*) Rotating disk electrode. Only the polished bottom surface of the electrode, which is typically 5 mm in diameter, contacts the solution. (*b*) Schematic concentration profile of analyte near the surface of the rotating disk electrode when the potential is great enough to reduce the concentration of analyte to 0 at the electrode surface.

The rate at which analyte diffuses from bulk solution to the surface of the electrode is proportional to the concentration difference between the two regions:

The symbol $\propto$ means "is proportional to."

$$\text{Current} \propto \text{rate of diffusion} \propto [C]_0 - [C]_s \qquad \textbf{(16-18)}$$

where $[C]_0$ is the concentration in bulk solution and $[C]_s$ is the concentration at the surface of the electrode. At sufficiently great potential, the rate of reaction at the electrode is so fast that $[C]_s \ll [C]_0$ and Equation 16-18 reduces to

$$\text{Limiting current} = \text{diffusion current} \propto [C]_0 \qquad \textbf{(16-19)}$$

The limiting current is called the **diffusion current** because it is governed by the rate at which analyte can diffuse to the electrode. The proportionality of diffusion current to bulk-solute concentration is the basis for quantitative analysis by amperometry and, in the next section, voltammetry.

The faster a rotating disk electrode spins, the thinner is the diffusion layer in Figure 16-13b and the greater is the diffusion current. A rapidly rotating Pt electrode can measure 20 nM H_2O_2 in rainwater.[21] H_2O_2 is oxidized to O_2 at +0.4 V (versus S.C.E.) at the Pt surface, and the current is proportional to $[H_2O_2]$ in the rainwater.

16-5 Voltammetry

Voltammetry is a collection of techniques in which the relation between current and voltage is observed during electrochemical processes.[22] The **voltammogram** in Figure 16-14a is a graph of current versus working electrode potential for a mixture of ferricyanide and ferrocyanide being oxidized or reduced at a rotating disk electrode. By convention, current is positive when analyte is reduced at the working electrode. The limiting (diffusion) current for oxidation of $Fe(CN)_6^{4-}$ is observed at potentials above +0.5 V (versus S.C.E.).

$$\underset{\substack{\text{Ferrocyanide}\\ \text{Fe(II)}}}{Fe(CN)_6^{4-}} \rightarrow \underset{\substack{\text{Ferricyanide}\\ \text{Fe(III)}}}{Fe(CN)_6^{3-}} + e^-$$

In this region, current is governed by the rate at which $Fe(CN)_6^{4-}$ diffuses to the electrode. Diffusion current is proportional to the bulk concentration of $Fe(CN)_6^{4-}$ (Figure 16-14b) just as it is for the rotating disk electrode in Equation 16-19. Below 0 V, there is another plateau corresponding to the diffusion current for reduction of $Fe(CN)_6^{3-}$, whose concentration is constant in all the solutions.

Polarography has been largely replaced by voltammetry with electrodes that do not present the toxicity hazard of Hg. Mercury is still the electrode of choice for stripping analysis, which is the most sensitive voltammetric technique. For cleaning up Hg spills, see note 23.

Polarography

Voltammetry conducted with a **dropping-mercury electrode** is called **polarography** (Figure 16-15). The dispenser suspends one drop of mercury from the bottom of the capillary. After current and voltage are measured, the drop is mechanically dislodged. Then a

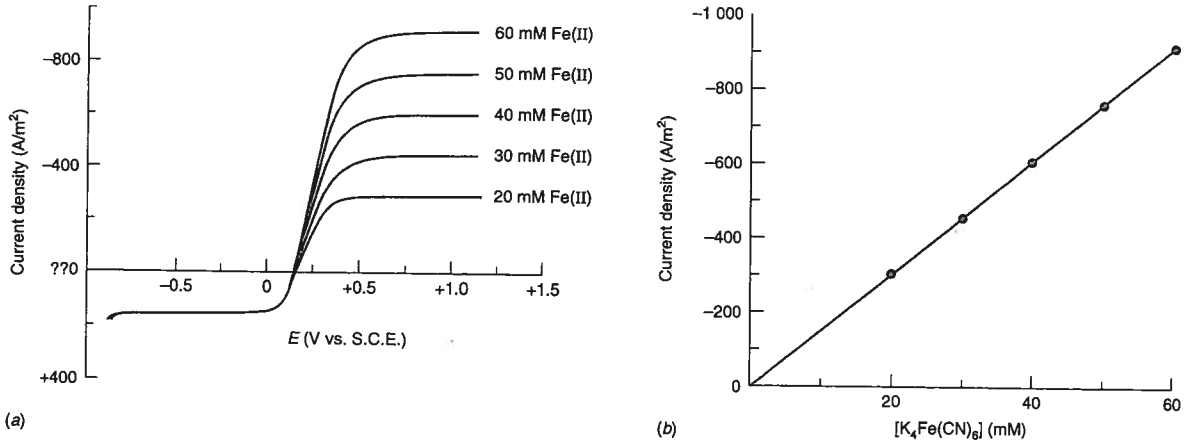


FIGURE 16-14 (*a*) Voltammograms for a mixture of 10 mM $K_3Fe(CN)_6$ and 20–60 mM $K_4Fe(CN)_6$ in 0.1 M Na_2SO_4 at a glassy carbon rotating electrode. Rotation speed = 2 000 revolutions/min and voltage sweep rate = 5 mV/s. (*b*) Dependence of limiting current on $K_4Fe(CN)_6$ concentration. [From J. Nikolic, E. Expósito, J. Iniesta, J. González-Garcia, and V. Montiel, "Theoretical Concepts and Applications of a Rotating Disk Electrode," *J. Chem. Ed.* 2000, *77*, 1191.]

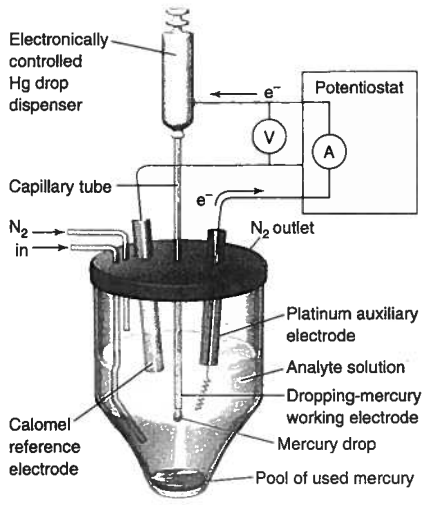


FIGURE 16-15 Polarography apparatus featuring a dropping-mercury working electrode. Polarography was invented by J. Heyrovský in 1922, for which he received the Nobel Prize in 1959.

fresh drop is suspended and the next measurement is made. Freshly exposed Hg yields reproducible current-potential behavior. The current for other electrodes, such as Pt, depends on surface condition.

Most reactions studied with the Hg electrode are reductions. At a Pt surface, reduction of H^+ competes with reduction of many analytes:

$$2H^+ + 2e^- \rightarrow H_2(g) \qquad E^\circ = 0$$

Table 16-1 showed that there is a large *overpotential* for reduction of H^+ at the Hg surface. Reactions that are thermodynamically less favorable than reduction of H^+ can be carried out without competitive reduction of H^+. In neutral or basic solutions, even alkali metal (Group 1) cations are reduced more easily than H^+. Furthermore, reduction of a metal into a mercury *amalgam* is more favorable than reduction to the solid state:

An **amalgam** is anything dissolved in Hg.

$$K^+ + e^- \rightarrow K(s) \qquad E^\circ = -2.936\ V$$
$$K^+ + e^- + Hg \rightarrow K(in\ Hg) \qquad E^\circ = -1.975\ V$$

Mercury is not useful for studying oxidations because Hg is oxidized in noncomplexing media near +0.25 V (versus S.C.E.). If the concentration of Cl^- is 1 M, Hg is oxidized near 0 V because Hg(II) is stabilized by Cl^-:

$$Hg(l) + 4Cl^- \rightleftharpoons HgCl_4^{2-} + 2e^-$$

For oxidations, Pt, Au, C, or diamond working electrodes in appropriate solvents provide a range of accessible potentials (Table 16-2). Boron-doped chemical-vapor-deposited diamond (Figure 16-16) is an exceptionally inert carbon electrode with a wide potential window, low background current,[24] and visible and infrared transparency.

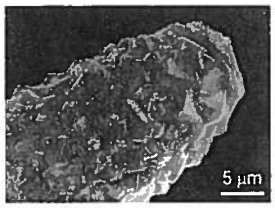


FIGURE 16-16 Boron-doped diamond coating on Pt electrode. [From J. Cvačka et al., *Anal. Chem.* 2003, *75*, 2678. Courtesy G. M. Swain, Michigan State University.]

TABLE 16-2 Approximate working electrode potential range in 1 M H_2SO_4

Electrode	Potential range (V vs. S.C.E.)
Pt	−0.2 to +0.9 V
Au	−0.3 to +1.4 V
Hg	−1.3 to +0.1 V
Glassy carbon	−0.8 to +1.1 V
B-doped diamond[a]	−1.5 to +1.7 V
Fluorinated B-doped diamond[b]	−2.5 to +2.5 V

a. A. E. Fischer, Y. Show, and G. M. Swain, "Electrochemical Performance of Diamond Thin-Film Electrodes from Different Commercial Sources," Anal. Chem. 2004, 76, 2553; Y. Dai, G. M. Swain, M. D. Porter, and J. Zak, "Optically Transparent Carbon Electrodes," Anal. Chem. 2008, 80, 14; J. Stotter, Y. Show, S. Wang, and G. Swain, "Comparison of Electrical, Optical, and Electrochemical Properties of Diamond and Indium Tin Oxide Thin-Film Electrodes," Chem. Mater. 2005, 17, 4880.

b. S. Ferro and A. De Battisti, "The 5-V Window of Polarizability of Fluorinated Diamond Electrodes in Aqueous Solution," Anal. Chem. 2003, 75, 7040.

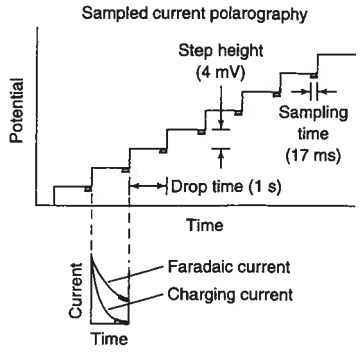


FIGURE 16-17 *Staircase voltage profile* used in *sampled current polarography.* Current is measured only during the intervals shown by heavy, colored lines. Potential is scanned toward more negative values as the experiment progresses. Lower graph shows that charging current decays more rapidly than faradaic current after each voltage step.

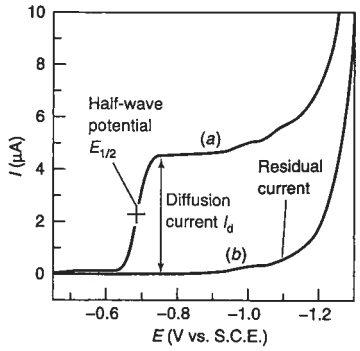


FIGURE 16-18 *Sampled current polarograms* of (*a*) 5 mM Cd^{2+} in 1 M HCl and (*b*) 1 M HCl alone.

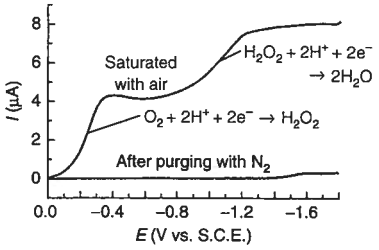


FIGURE 16-19 Sampled current polarogram of 0.1 M KCl, saturated with air or purged (bubbled) with N_2 to remove O_2.

Polarograms in the older literature have large oscillations superimposed on the wave in Figure 16-18a. For the first 50 years of polarography, current was measured continuously as Hg flowed from a capillary tube. Each drop grew until it fell off and was replaced by a new drop. The current oscillated from a low value when the drop was small to a high value when the drop was big.

One way to conduct a measurement is by **sampled current polarography** with the *staircase voltage ramp* in Figure 16-17. After each drop of Hg is dispensed, the potential is made more negative by 4 mV. After waiting almost 1 s, current is measured during the last 17 ms of the life of each Hg drop. The **polarographic wave** in Figure 16-18a results from reduction of Cd^{2+} analyte to form an amalgam:

$$Cd^{2+} + 2e^- \rightarrow Cd(in\ Hg)$$

The potential at which half the maximum current is reached in Figure 16-18a, called the **half-wave potential** ($E_{1/2}$), is characteristic of a given analyte in a given medium and can be used for qualitative analysis. For electrode reactions in which reactants and products are both in solution, such as $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$, $E_{1/2}$ (expressed with respect to S.H.E.) is nearly equal to E° for the half-reaction.

For quantitative analysis, the *diffusion current* in the plateau region is proportional to the concentration of analyte. Diffusion current is measured from the baseline recorded without analyte in Figure 16-18b. **Residual current** in the absence of analyte is due to reduction of impurities in solution and on the surface of the electrodes. Near −1.2 V in Figure 16-18, current increases rapidly as reduction of H^+ to H_2 commences.

For quantitative analysis, the limiting current should be controlled by the rate at which analyte can diffuse to the electrode. We minimize convection by using an unstirred solution. We minimize migration (electrostatic attraction of analyte) by using a high concentration of *supporting electrolyte*, such as 1 M HCl in Figure 16-18.

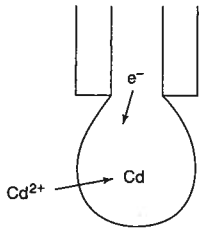
Oxygen must be absent because O_2 gives two polarographic waves when it is reduced to H_2O_2 and then to H_2O (Figure 16-19). Typically, N_2 is bubbled through analyte solution for 10 min to remove O_2.[25] Then N_2 flow in the gas phase is continued to keep O_2 out. The liquid should not be purged with N_2 during a measurement, because we do not want convection of analyte to the electrode.

Faradaic and Charging Currents

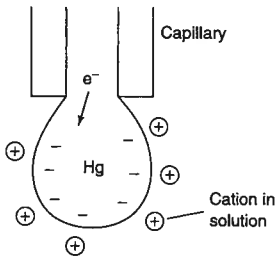
The current we seek to measure in voltammetry is **faradaic current** due to reduction or oxidation of analyte at the working electrode. In Figure 16-18a, faradaic current comes from reduction of Cd^{2+} at the Hg electrode. Another current, called **charging current** (or *capacitor current* or *condenser current*) interferes with every measurement. We step the working electrode to a more negative potential by forcing electrons into the electrode from the potentiostat. In response, cations in solution flow toward the electrode, and anions flow away from the electrode (Box 16-3). This flow of ions and electrons, called *charging current*, is not from redox reactions. We try to minimize charging current, which obscures faradaic current. Charging current usually controls the detection limit in voltammetry.

The bottom of Figure 16-17 shows the behavior of faradaic and charging currents after each potential step. Faradaic current decays because analyte cannot diffuse to the electrode

Faradaic current: due to redox reaction at the electrode



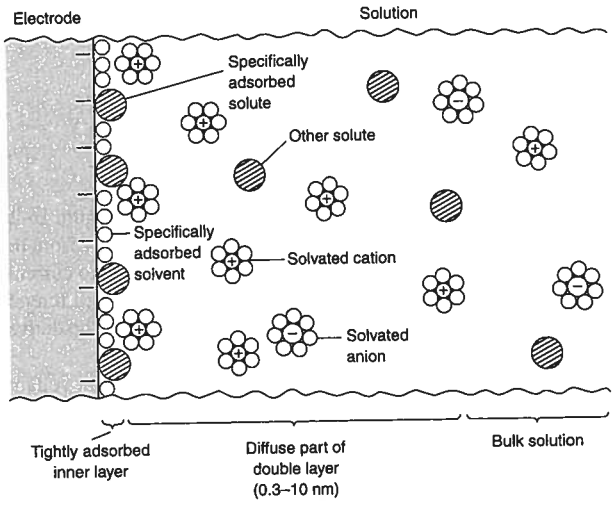
Charging current: due to electrostatic attraction or repulsion of ions in solution and electrons in the electrode



Faradaic current is the signal of interest. Charging current obscures the signal of interest, so we seek to minimize charging current.

BOX 16-3 The Electric Double Layer

When a power supply pumps electrons into or out of an electrode, the charged surface of the electrode attracts ions of opposite charge. The charged electrode and the oppositely charged ions next to it constitute the **electric double layer.**



Electrode-solution interface. The tightly adsorbed inner layer (also called the *compact, Helmholtz,* or *Stern* layer) may include solvent and any solute molecules. Cations in the inner layer do not completely balance the charge of the electrode. Therefore, excess cations are required in the *diffuse part of the double layer* for charge balance.

A given solution has a *potential of zero charge* at which there is no excess charge on the electrode. This potential is −0.58 V (versus a calomel electrode containing 1 M KCl) for a mercury electrode immersed in 0.1 M KBr. It shifts to −0.72 V for the same electrode in 0.1 M KI.

The first layer of molecules at the surface of the electrode is *specifically adsorbed* by van der Waals and electrostatic forces. The adsorbed solute could be neutral molecules, anions, or cations. Iodide is more strongly adsorbed than bromide, so the potential of zero charge for KI is more negative than for KBr: A more negative potential is required to expel adsorbed iodide from the electrode surface.

The next layer beyond the specifically adsorbed layer is rich in cations attracted by the negative electrode. The excess of cations decreases with increasing distance from the electrode. This region, whose composition is different from that of bulk solution, is called the *diffuse part of the double layer* and is typically 0.3–10 nm thick. The thickness is controlled by the balance between attraction toward the electrode and randomization by thermal motion.

When a species is created or destroyed by an electrochemical reaction, its concentration near the electrode is different from its concentration in bulk solution (Figure 16-13b and Color Plate 11). The region containing excess product or decreased reactant is called the *diffusion layer* (not to be confused with the diffuse part of the double layer).

fast enough to sustain the high reaction rate. Charging current decays even faster because ions near the electrode redistribute themselves rapidly. A second after each potential step, faradaic current is still significant and charging current is small.

Square Wave Voltammetry

The most efficient voltage profile for voltammetry, called **square wave voltammetry,** uses the waveform in Figure 16-20, which consists of a square wave superimposed on a staircase.[26] During each cathodic pulse, analyte is reduced at the electrode surface. During the anodic

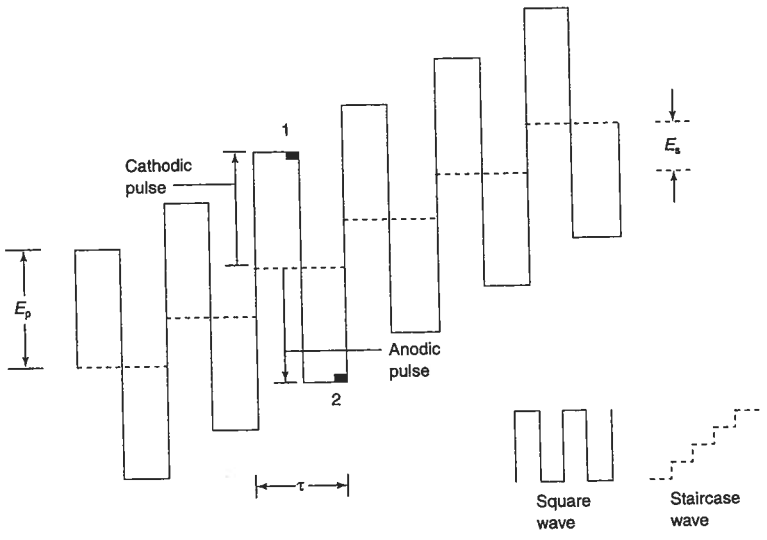


FIGURE 16-20 Waveform for square wave voltammetry. Typical parameters are pulse height (E_p) = 25 mV, step height (E_s) = 10 mV, and pulse period (τ) = 5 ms. Current is measured in regions 1 and 2. Optimum values are $E_p = 50/n$ mV and $E_s = 10/n$ mV, where n is the number of electrons in the half-reaction.

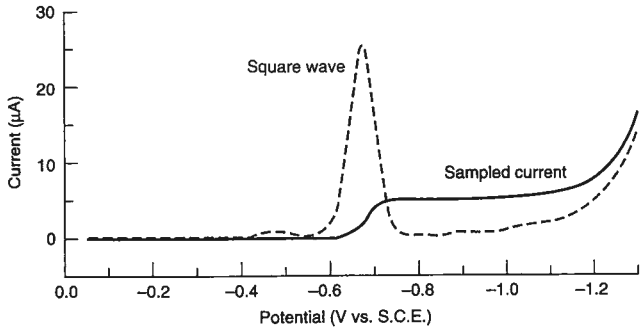


FIGURE 16-21 Comparison of polarograms of 5 mM Cd^{2+} in 1 M HCl. Waveforms are shown in Figures 16-17 and 16-20. Sampled current: drop time = 1 s, step height = 4 mV, sampling time = 17 ms. Square wave: drop time = 1 s, step height = 4 mV, pulse period = 67 ms, pulse height = 25 mV, sampling time = 17 ms.

pulse, analyte that was just reduced is reoxidized. The square wave polarogram in Figure 16-21 is the *difference* in current between intervals 1 and 2 in Figure 16-20. Electrons flow from the electrode to analyte at point 1 and in the reverse direction at point 2. Because the two currents have opposite signs, their difference is larger than either current alone. When the difference is plotted, the shape of the square wave polarogram in Figure 16-21 is essentially the derivative of the sampled current polarogram.

Advantages of square wave voltammetry:

- increased signal
- derivative (peak) shape permits better resolution of neighboring signals
- faster measurement

The signal in square wave voltammetry is increased relative to a sampled current voltammogram and the wave becomes peak shaped. Signal is increased because reduced product from each cathodic pulse is right at the surface of the electrode waiting to be oxidized by the next anodic pulse. Each anodic pulse provides a high concentration of reactant at the surface of the electrode for the next cathodic pulse. The detection limit is reduced from ~10^{-5} M for sampled current voltammetry to ~10^{-7} M in square wave voltammetry. Because it is easier to resolve neighboring peaks than neighboring waves, square wave voltammetry can resolve species whose half-wave potentials differ by ~0.05 V, whereas potentials must differ by ~0.2 V to be resolved in sampled current voltammetry. Square wave voltammetry is faster than other voltammetric techniques. The square wave polarogram in Figure 16-21 was recorded in one-fifteenth of the time required for the sampled current polarogram. In principle, the shorter the pulse period, τ, in Figure 16-20, the greater the current that will be observed. With τ = 5 ms (a practical lower limit) and E_s = 10 mV, an entire square wave polarogram with a 1-V width is obtained with *one drop of Hg in 0.5 s*. Such rapid sweeps allow voltammograms to be recorded on individual components as they emerge from a chromatography column.

Anodic stripping analysis:

1. Concentrate analyte onto electrode by reduction
2. Reoxidize analyte by scanning to more positive potential
3. Peak current during oxidation is proportional to analyte concentration

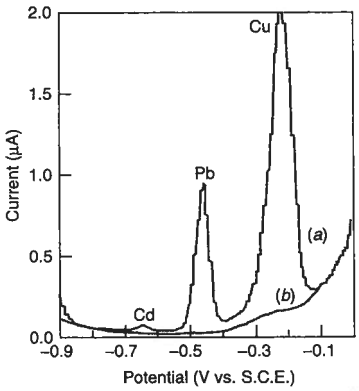


FIGURE 16-22 (*a*) Anodic stripping voltammogram of honey dissolved in water and acidified to pH 1.2 with HCl. Cd, Pb, and Cu were reduced from solution into a thin film of Hg for 5 min at −1.4 V (versus S.C.E.) prior to recording the voltammogram. (*b*) Voltammogram obtained without 5-min reduction step. The concentrations of Cd and Pb in the honey were 7 and 27 ng/g (ppb), respectively. Precision was 2–4%. [From Y. Li, F. Wahdat, and R. Neeb, "Digestion-Free Determination of Heavy Metals in Honey," *Fresenius J. Anal. Chem.* 1995, *351*, 678.]

Stripping Analysis

In **stripping analysis,** analyte from a dilute solution is concentrated into a thin film of Hg or other electrode material, usually by electroreduction. The electroactive species is then *stripped* from the electrode by reversing the direction of the voltage sweep. The potential becomes more *positive*, *oxidizing* the species back into solution. Peak current measured during oxidation is proportional to the quantity of analyte that was deposited. Figure 16-22 shows an anodic stripping voltammogram of Cd, Pb, and Cu from honey.

Stripping is the most sensitive voltammetric technique (Table 16-3), because analyte is concentrated from a dilute solution. The longer the period of concentration, the more sensitive

TABLE 16-3 Detection limits for stripping analysis

Analyte	Stripping mode	Detection limit
Ag^+	Anodic	2×10^{-12} M[a]
Testosterone	Anodic	2×10^{-10} M[b]
I^-	Cathodic	1×10^{-10} M[c]
DNA or RNA	Cathodic	2–5 pg/mL[d]
Fe^{3+}	Cathodic	1×10^{-11} M[e]

a. S. Dong and Y. Wang, Anal. Chim. Acta 1988, 212, 341.

b. J. Wang, "Adsorptive Stripping Voltammetry." EG&G Princeton Applied Research Application Note A-7 (1985).

c. G. W. Luther III, C. Branson Swartz, and W. J. Ullman, Anal. Chem. 1988, 60, 1721. I^- is deposited onto the mercury drop by anodic oxidation: $Hg(l) + I^- \rightleftharpoons \frac{1}{2}Hg_2I_2(adsorbed\ on\ Hg) + e^-$.

d. S. Reher, Y. Lepka, and G. Schwedt, Fresenius J. Anal. Chem. 2000, 368, 720; J. Wang, Anal. Chim. Acta 2003, 500, 247.

e. C. M. G. van den Berg, Anal. Chem. 2006, 78, 156.

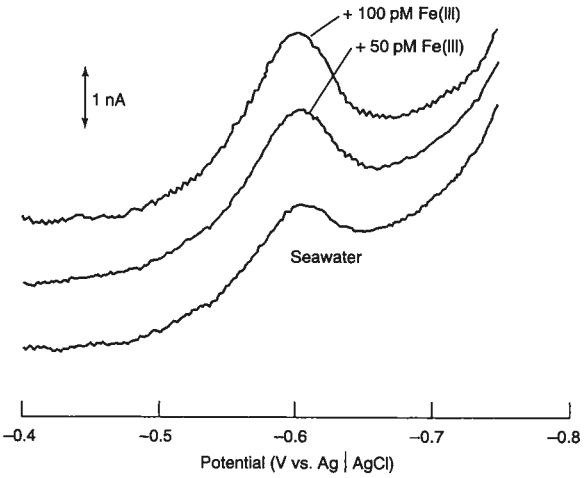
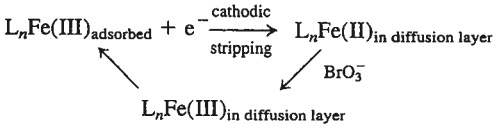


FIGURE 16-23 Sampled current cathodic stripping voltammogram of Fe(III) in seawater plus two standard additions of 50 pM Fe(III). [From H. Obata and C. M. G. van den Berg, "Determination of Picomolar Levels of Iron in Seawater Using Catalytic Cathodic Stripping Voltammetry," *Anal. Chem.* 2001, *73*, 2522. See also C. M. G. van den Berg, "Chemical Speciation of Iron in Seawater by Cathodic Stripping Voltammetry with Dihydroxynaphthalene," *Anal. Chem.* 2006, *78*, 156.]

is the analysis. Only a fraction of analyte from the solution is deposited, so deposition must be done for a reproducible time (such as 5 min) with reproducible stirring.

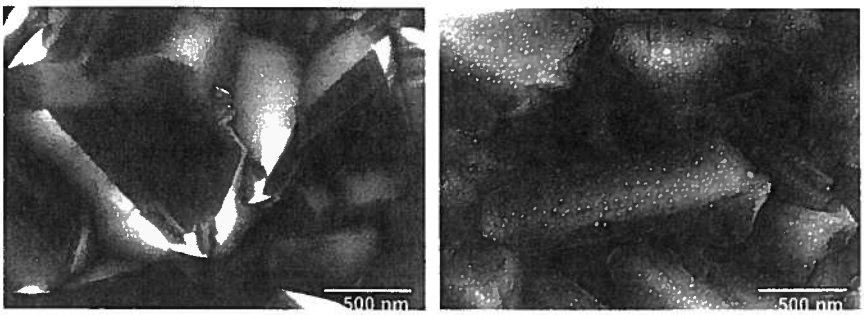
The detection limit for Fe(III) in seawater can be reduced to 10^{-11} M with a *catalytic stripping* process. First, 20 μM 2,3-dihydroxynaphthalene (L), 20 mM bromate (BrO_3^-) and pH 8.0 buffer are added to seawater that has been purged with N_2 to remove O_2. Dihydroxynaphthalene forms a complex, $L_nFe(III)$, which adsorbs onto a mercury drop electrode poised at −0.1 V versus Ag | AgCl during 60 s of vigorous stirring. After stirring is stopped and the solution becomes stationary, the potential is scanned from −0.1 to −0.8 V to give the lower trace in Figure 16-23. At −0.6 V, Fe(III) is reduced to Fe(II), which begins to diffuse away from the electrode. Before Fe(II) goes very far, BrO_3^- oxidizes Fe(II) back to Fe(III), which is readsorbed and available to be reduced again. The cathodic stripping current is 290 times greater in the presence of 20 mM BrO_3^- than without BrO_3^-. Fe(II) is a catalyst for the net reduction of BrO_3^-.



Rigorous precautions must be taken to remove iron from reagents and equipment when measuring concentrations of 10^{-11} M. For example, 3 M KCl in the salt bridge had to be purified, and the bridge itself was made of Teflon instead of glass.

Electrodes other than mercury can be used for stripping analysis if there is a means to adsorb analyte on the electrode. Traces of As(III) can be measured by codeposition with gold on a boron-doped diamond electrode. Pure diamond is an electrical insulator. Conductive boron-doped diamond can be grown on Si by gas-phase decomposition of 0.5 vol% CH_4 with 10 ppm B_2H_6 (diborane) in a 0.06-bar H_2 atmosphere at 800°C in a microwave plasma.

Figure 16-24a shows the bare surface of boron-doped diamond. Figure 16-24b shows the surface after 90 s of deposition at −0.45 V (vs. Ag | AgCl) from 10 ppm As(III) + 10 ppm



2,3-Dihydroxynaphthalene

(Presumably, the polarizable pi electron cloud of naphthalene is bound to the polarizable Hg by van der Waals forces)

(*a*) (*b*)

FIGURE 16-24 Scanning electron micrographs of (*a*) bare boron-doped diamond electrode surface and (*b*) diamond surface with Au_xAs_y nanoparticles deposited at −0.45 V in 90 s from 10 ppm As(III) + 10 ppm Au(III) in 1 M HCl. [From Y. Song and G. M. Swain, "Development of a Method for Total Inorganic Arsenic Analysis Using Anodic Stripping Voltammetry and a Au-coated, Diamond Thin-Film Electrode," *Anal. Chem.* 2007, *79*, 2412.]

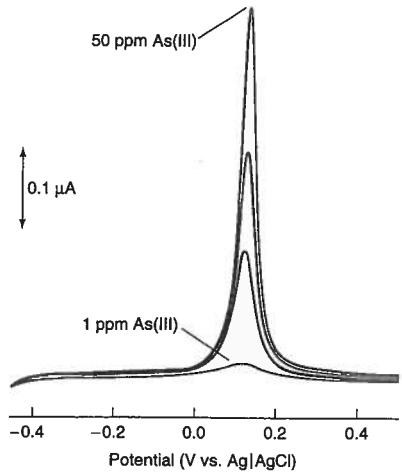


FIGURE 16-25 Anodic stripping of As(III) from a boron-doped diamond electrode. Au_xAs_y was deposited from a solution containing 100 ppm Au(III) in 1 M HCl. Peak current is proportional to the concentration of As(III) in the deposition solution. [From Y. Song and G. M. Swain, "Development of a Method for Total Inorganic Arsenic Analysis Using Anodic Stripping Voltammetry and a Au-coated, Diamond Thin-Film Electrode," *Anal. Chem.* 2007, *79*, 2412.]

Au(III) in 1 M HCl. An intermetallic Au_xAs_y compound has been deposited as particles with a mean diameter of 22 nm. No As is deposited in the absence of gold. After deposition, the potential is scanned to positive values to oxidize As back to As(III) (Figure 16-25). The peak current observed at +0.16 V is proportional to the As(III) analyte concentration in the original solution. Finally, the potential is held at +0.6 V to oxidize all As and Au off the electrode before beginning a new analysis.

The detection limit for As(III) is 0.005 ppb = 7×10^{-11} M. As(V) cannot be measured directly, but it can be quantitatively reduced to As(III) with sodium sulfite (Na_2SO_3) in HCl. The resulting As(III) can be measured by stripping analysis. A solution containing both As(III) and As(V) can be analyzed by first measuring As(III) on one aliquot. Then the As(V) is reduced in a second aliquot, and total As in the second aliquot is measured by stripping.

Boron-doped diamond is an especially useful electrode because its surface is stable over a wide potential range and is not altered from one analysis to the next. It does not adsorb polar molecules that might interfere with deposition of analyte. Diamond has an exceptionally wide potential limit (−1.5 to +1.7 V vs. S.C.E.) and gives exceptionally low background currents in the absence of analyte.

Cyclic Voltammetry

In **cyclic voltammetry,** we apply the triangular waveform in Figure 16-26 to the working electrode. After the application of a linear voltage ramp between times t_0 and t_1 (typically a few seconds), the ramp is reversed to bring the potential back to its initial value at time t_2. The cycle might be repeated many times.

The initial portion of the cyclic voltammogram in Figure 16-27, beginning at t_0, exhibits a *cathodic wave*. Instead of leveling off at the top of the wave, current decreases at more negative potential because analyte becomes depleted near the electrode. Diffusion is too slow to replenish analyte near the electrode. At the time of peak voltage (t_1), the cathodic current has decayed to a small value. After t_1, the potential is reversed and, eventually, reduced product near the electrode is oxidized. This reaction produces an *anodic wave*. Finally, as the reduced product is depleted, the anodic current decays back toward its initial value at t_2.

Figure 16-27a illustrates a *reversible* reaction that is fast enough to maintain equilibrium concentrations of reactant and product *at the electrode surface*. The peak anodic and peak cathodic currents have equal magnitudes in a reversible process, and

$$E_{pa} - E_{pc} = \frac{2.22RT}{nF} = \frac{57.0}{n}(\text{mV}) \quad (\text{at } 25°\text{C}) \qquad (16\text{-}20$$

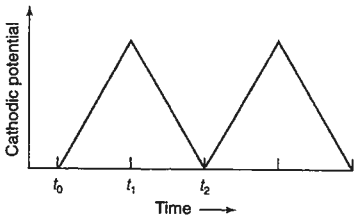


FIGURE 16-26 Waveform for cyclic voltammetry. Corresponding times are indicated in Figure 16-27.

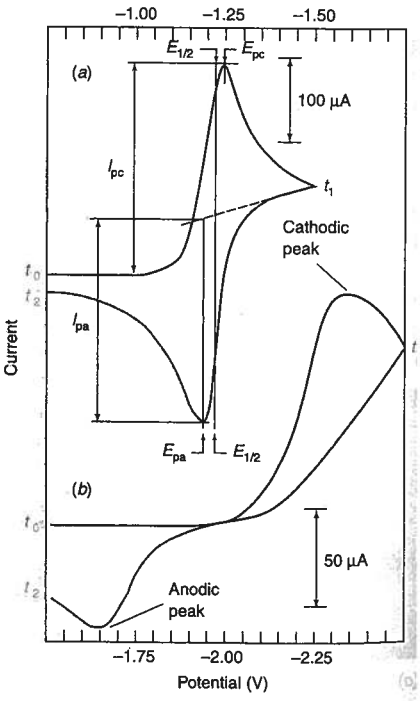


FIGURE 16-27 Cyclic voltammograms of (*a*) 1 mM O_2 in acetonitrile with 0.10 M $(C_2H_5)_4N^+ClO_4^-$ electrolyte and (*b*) 0.060 mM 2-nitropropane in acetonitrile with 0.10 M $(n\text{-}C_7H_{15})_4N^+ClO_4^-$ electrolyte. The reaction in curve *a* is

$$O_2 + e^- \rightleftharpoons \underset{\text{Superoxide}}{O_2^-}$$

Working electrode, Hg; reference electrode, Ag | 0.001 M $AgNO_3(aq)$ | 0.10 M $(C_2H_5)_4N^+ClO_4^-$ in acetonitrile; scan rate = 100 V/s. I_{pa} is the peak anodic current and I_{pc} is the peak cathodic current. E_{pa} and E_{pc} are the potentials at which these currents are observed. [From D. H. Evans, K. M. O'Connell, R. A. Petersen, and M. J. Kelly, "Cyclic Voltammetry," *J. Chem. Ed.* 1983, *60*, 290.]

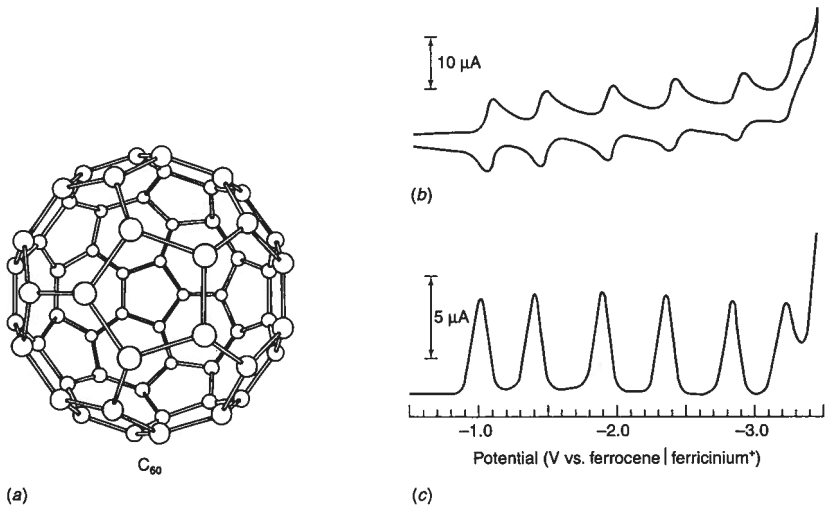


FIGURE 16-28 (*a*) Structure of C_{60} (buckminsterfullerene). (*b*) Cyclic voltammetry and (*c*) polarogram of 0.8 mM C_{60}, showing six waves for reduction to C_{60}^-, C_{60}^{2-}, . . . , C_{60}^{6-}. The acetonitrile/toluene solution was at −10°C with $(n\text{-}C_4H_9)_4N^+PF_6^-$ supporting electrolyte. The reference electrode contains the ferrocene | ferricinium$^+$ redox couple. Ferrocene is $(C_5H_5)_2Fe$ and ferricinium cation is $(C_5H_5)_2Fe^+$. The structure of ferrocene was shown in Reaction 16-15. [From Q. Xie, E. Pérez-Cordero, and L. Echegoyen, "Electrochemical Detection of C_{60}^{6-} and C_{70}^{6-}," *J. Am. Chem. Soc.* **1992**, *114*, 3978.]

where E_{pa} and E_{pc} are the potentials at which the *p*eak *a*nodic and *p*eak *c*athodic currents are observed and n is the number of electrons in the half-reaction. The half-wave potential, $E_{1/2}$, lies midway between the two peak potentials. Figure 16-27b is the cyclic voltammogram of an *irreversible* reaction. The cathodic and anodic peaks are broader and more separated. At the limit of irreversibility, where oxidation is very slow, no anodic peak is seen.

For a reversible reaction, the peak current (I_{pc}, amperes) for the forward sweep of the first cycle is proportional to the concentration of analyte and the square root of sweep rate:

$$I_{pc} = (2.69 \times 10^8) n^{3/2} A C D^{1/2} \nu^{1/2} \qquad \text{(at 25°C)} \qquad \textbf{(16-21)}$$

where n is the number of electrons in the half-reaction, A is the area of the electrode (m^2), C is the concentration (mol/L), D is the diffusion coefficient of the electroactive species (m^2/s), and ν is sweep rate (V/s). The faster the sweep rate, the greater the peak current, as long as the reaction remains reversible. If the electroactive species is adsorbed on the electrode, the peak current is proportional to ν rather than $\sqrt{\nu}$.

For catalytic stripping in Figure 16-23, current was proportional to $\sqrt{\nu}$, consistent with the rate-limiting step being diffusion of BrO_3^- to the electrode. If the rate-limiting step were reduction of Fe(III) adsorbed on the electrode, the peak current would have been proportional to ν.

Cyclic voltammetry is used to characterize the redox behavior of compounds such as C_{60} in Figure 16-28 and to elucidate the kinetics of electrode reactions.[27]

Microelectrodes

Microelectrodes have working dimensions from a few tens of micrometers down to nanometers.[28] The surface area of the electrode is small, so the current is tiny. With a small current, the ohmic drop (= IR) in a highly resistive medium is small, thus allowing microelectrodes to be used in poorly conducting nonaqueous media (Figure 16-29). The electric

Advantages of ultramicroelectrodes:

- Fit into small places
- Useful in resistive, nonaqueous media (because of small ohmic losses)
- Rapid voltage scans (possible because of small double-layer capacitance) allow short-lived species to be studied
- Detection limits increased by orders of magnitude because of low charging current

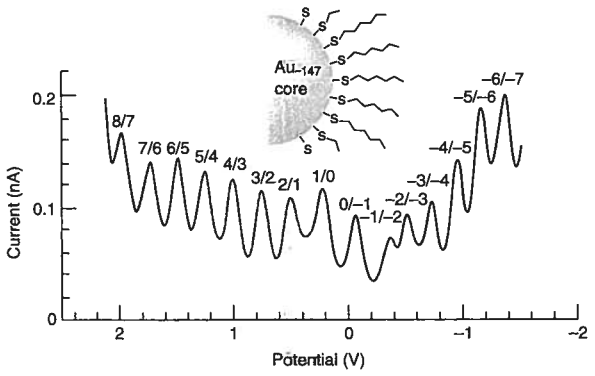
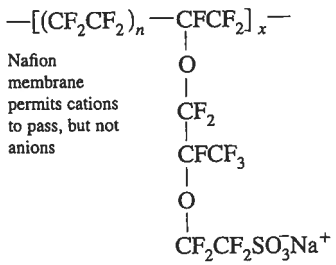
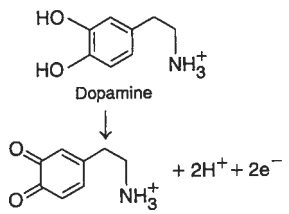


FIGURE 16-29 Voltammogram of gold nanoparticles ($Au_{\sim 147}$ capped with ~50 hexanethiol molecules) in 1,2-dichloroethane solution recorded with 25-μm-diameter Pt working electrode. The nanoparticle exhibits oxidation states from −7 to +8 over the potential range of this scan. Supporting electrolyte: 10 mM $[(C_6H_5)_3P{=}N{=}P(C_6H_5)_3]^+[(C_6F_5)_4B]^-$. Potential measured versus "quasi-reference" electrode—a silver wire whose potential is ~0.1 V versus Ag | AgCl. [From B. M. Quinn, P. Liljeroth, V. Ruiz, T. Laaksonen, and K. Kontturi, "Electrochemical Resolution of 15 Oxidation States for Monolayer Protected Gold Nanoparticles," *J. Am. Chem. Soc.* **2003**, *125*, 6644.]





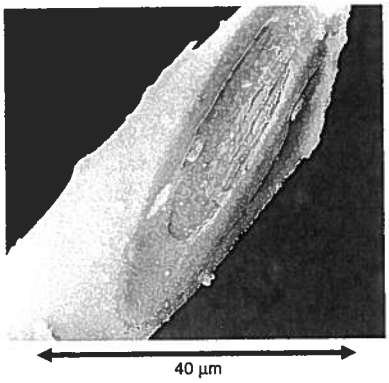


FIGURE 16-30 Electron micrograph of the tip of a Nafion-coated carbon-fiber electrode. The carbon inside the electrode has a diameter of 10 μm. Nafion permits cations to pass but excludes anions. [Photo courtesy R. M. Wightman. From R. M. Wightman, L. J. May, and A. C. Michael, "Detection of Dopamine Dynamics in the Brain," *Anal. Chem.* 1988, *60*, 769A.]

capacitance of the double layer (Box 16-3) of a microelectrode is very small. Low capacitance gives low background charging current relative to the faradaic current of a redox reaction. The result is a lowering of the detection limit by as much as three orders of magnitude over conventional electrodes. Low capacitance also enables the potential to be varied at rates up to 500 kV/s, thus allowing short-lived species with lifetimes of less than 1 μs to be studied.

Sufficiently small electrodes fit inside a living cell. A carbon fiber coated with insulating polymer provides a 1-μm-diameter working electrode at the exposed tip. Carbon is fouled by adsorption of organic molecules inside living cells, so a thin layer of Pt or Au is electrolytically plated onto the exposed carbon. The metallized electrode is cleaned in situ (inside the cell during an experiment) by an anodic voltage pulse that desorbs surface-bound species and produces an oxide layer on the metal, followed by a cathodic pulse to reduce the oxide.[29]

Figure 16-30 shows a carbon fiber coated with a cation-exchange membrane called Nafion, which has fixed negative charges. Cations diffuse through the membrane, but anions are excluded. The electrode can measure the cationic neurotransmitter, dopamine, in a rat brain.[30] Negatively charged ascorbate, which ordinarily interferes with dopamine analysis, is excluded by Nafion. The response to dopamine is 1 000 times higher than the response to ascorbate.

Figure 16-31 shows an application of a microelectrode array in biology. Cells from a line called pheochromocytoma PC 12, derived from a tumor of the adrenal gland, release dopamine when stimulated by K^+. Neurotransmitters are contained in small intracellular compartments called *vesicles*. To release their content outside the cell, vesicles fuse with the cell membrane and open up. This process is called *exocytosis*. The microelectrode array consists of 5-μm-diameter carbon fibers in a seven-barrel glass capillary pulled to a fine point. Each carbon fiber in Figure 16-31a is an independent working electrode that can sample a region approximately 5 μm in diameter. Figure 16-31b shows the electrode pressed against a single cell, distorting the cell into a crescent shape. When 0.1 M KCl from the micropipette at the left in Figure 16-31b is injected into the medium, the cell releases dopamine in discrete exocytotic events. Figure 16-31c shows traces from electrodes A–G over 16 min during which KCl is injected every 45 s. All traces are different, indicating that different patches of cell surface respond differently. For example, patches near electrodes F and G are "cold" for the first 8 min—with little release of dopamine. Something changes after 8 min, and these two patches become "hot."

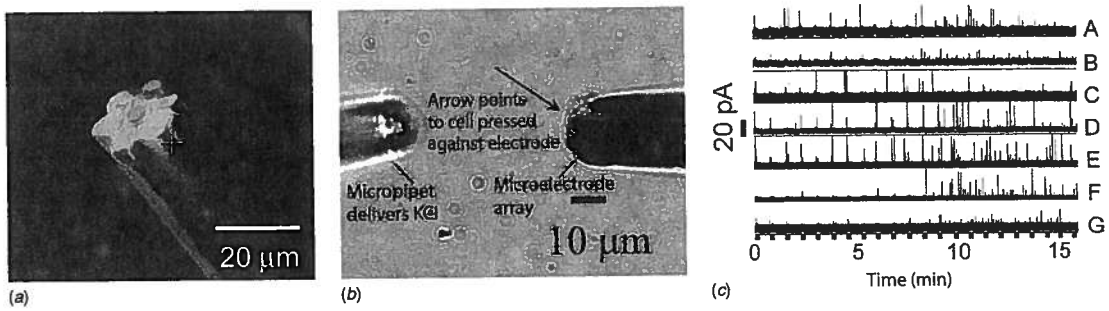


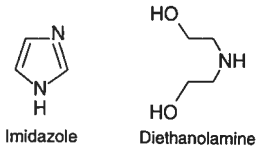
FIGURE 16-31 (*a*) Carbon-fiber microelectrode array with seven electrodes. (*b*) Microelectrode array (right) pressed against a PC 12 cell distorted into a crescent shape by the electrode. Micropipette at left is used to deliver 0.1 M KCl to stimulate dopamine release from the cell. A Ag|AgCl reference/auxiliary electrode is not visible. (*c*) Amperometric traces from all seven electrodes during exocytotic release of neurotransmitter. [From B. Zhang, K. L. Adams, S. J. Luber, D. J. Eves, M. L. Heien, and A. G. Ewing, "Spatially and Temporally Resolved Single-Cell Exocytosis Utilizing Individually Addressable Carbon Microelectrode Arrays," *Anal. Chem.* 2008, *80*, 1394.]

16-6 Karl Fischer Titration of H_2O

The **Karl Fischer titration,**[31] which measures traces of water in transformer oil, solvents, foods, polymers, and other substances, is performed half a million times each day.[32] The titration is usually performed by delivering titrant from an automated buret or by coulometric generation of titrant. The volumetric procedure tends to be appropriate for larger amounts of water (but can go as low as ~1 mg H_2O), and the coulometric procedure tends to be appropriate for smaller amounts of water.

We illustrate the coulometric procedure in Figure 16-32, in which the main compartment contains anode solution plus unknown. The smaller compartment at the left has an internal Pt electrode immersed in cathode solution and an external Pt electrode immersed in the anode solution of the main compartment. The two compartments are separated by an ion-permeable membrane. Two Pt electrodes are used for end-point detection.

Anode solution contains an alcohol, a base, SO_2, I^-, and possibly another organic solvent. Methanol and diethylene glycol monomethyl ether ($CH_3OCH_2CH_2OCH_2CH_2OH$) are typical alcohols. Typical bases are imidazole and diethanolamine. The organic solvent may contain chloroform, formamide, or other solvents. The trend is to avoid chlorinated solvents because of their environmental hazards. When analyzing nonpolar substances such as transformer oil, sufficient solvent, such as chloroform, should be used to make the reaction homogeneous. Otherwise, moisture trapped in oily emulsions is inaccessible. (An *emulsion* is a fine suspension of liquid-phase droplets in another liquid.)



Imidazole Diethanolamine

The anode at the lower left in Figure 16-32 generates I_2 by oxidation of I^-. In the presence of H_2O, reactions occur between the alcohol (ROH), base (B), SO_2, and I_2.

$$ROH + SO_2 + B \rightarrow BH^+ + ROSO_2^- \qquad \textbf{(16-22)}$$

$$H_2O + I_2 + ROSO_2^- + 2B \rightarrow ROSO_3^- + 2BH^+I^- \qquad \textbf{(16-23)}$$

The net reaction is oxidation of SO_2 by I_2, with formation of $ROSO_3^-$. One mole of I_2 is consumed for each mole of H_2O when the solvent is methanol. In other solvents, the stoichiometry can be more complex.[32]

Maintain pH in the range 4 to 7. Above pH 8, nonstoichiometric side reactions occur. Below pH 3, the reaction is slow.

In a typical procedure, the main compartment in Figure 16-32 is filled with anode solution and the coulometric generator is filled with cathode solution that may contain reagents designed to be reduced at the cathode. Current is run until moisture in the main compartment is consumed, as indicated by the end-point detection system described after the Example. An unknown is injected through the septum, and the coulometer is run again until moisture has been consumed. Two moles of electrons correspond to 1 mol of H_2O if the I_2:H_2O stoichiometry is 1:1.

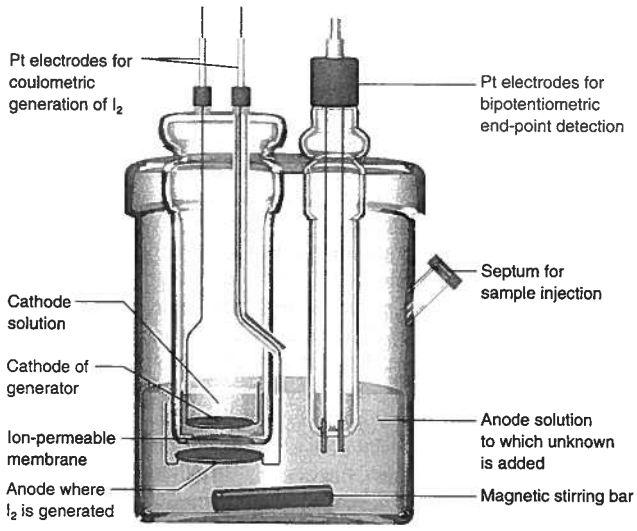
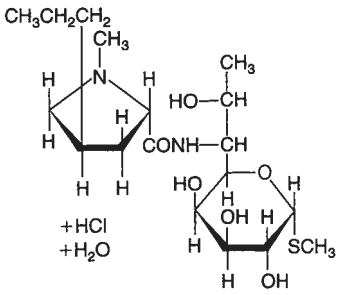


FIGURE 16-32 Apparatus for coulometric Karl Fischer titration.



Lincomycin hydrochloride monohydrate
$C_{18}H_{37}N_2O_7SCl$, FM 461.01
3.91 wt% H_2O

EXAMPLE **Standardization and Blank Correction in Karl Fischer Titration**

It is routine to standardize Karl Fischer reagents, or even a coulometer, with a standard such as lincomycin hydrochloride monohydrate, which contains 3.91 wt% H_2O. The coulometer is run until the end point is reached, indicating that the Karl Fischer reagent is dry. A port is opened briefly to add solid lincomycin, which is then titrated to the same end point. Then an unknown is added and titrated in the same manner. Find the wt% H_2O in the unknown.

Milligrams lincomycin	μg H_2O observed	μg H_2O theoretical	Difference (μg) = blank correction
3.89	172.4	152.1	172.4 − 152.1 = 20.3
13.64	556.3	533.3	556.3 − 533.3 = 23.0
19.25	771.4	752.7	771.4 − 752.7 = 18.7
			Average = 20.7

Milligrams unknown	μg H_2O observed	μg H_2O corrected (= observed − 20.7)	wt% H_2O in unknown
24.17	540.8	520.1	520.1 μg/24.17 mg = 2.15%
17.08	387.6	366.9	366.9 μg/17.08 mg = 2.15%

SOURCE: *Data from W. C. Schinzer, Pfizer Co., Michigan Pharmaceutical Sciences, Portage, MI.*

Solution For lincomycin, we observe ~20.7 μg more H_2O than expected, *independent of the sample size*. Excess H_2O comes from the atmosphere when the port is opened to add solid. To determine moisture in unknowns, subtract this blank from the total moisture titrated. This procedure can generate very reproducible data.

Test Yourself Observed H_2O in 20.33 mg of unknown was 888.8 μg. Apply the correction and find wt% H_2O in the unknown. (***Answer:*** 4.27%)

A **bipotentiometric** measurement is the most common way to detect the end point of a Karl Fischer titration. The detector circuit maintains a *constant current* (usually 5 or 10 μA) between the two detector electrodes at the right in Figure 16-32 while measuring the voltage needed to sustain the current. Prior to the equivalence point, the solution contains I^-, but little I_2 (which is consumed in Reaction 16-23 as fast as it is generated). To maintain a current of 10 μA, the cathode potential must be negative enough to reduce some component of the solvent system. At the equivalence point, excess I_2 suddenly appears and current can be carried at very low voltage by Reactions 16-24 and 16-25. The abrupt voltage drop marks the end point.

Cathode: $I_3^- + 2e^- \rightarrow 3I^-$ (16-24)

Anode: $3I^- \rightarrow I_3^- + 2e^-$ (16-25)

A trend in Karl Fischer coulometric instrumentation is to eliminate the separate cathode compartment in Figure 16-32 to reduce conditioning time required before samples can be analyzed and to eliminate clogging of the membrane.[33] The challenge is to minimize interference by products of the cathodic reaction.

End points in Karl Fischer titrations tend to drift because of slow reactions and water leaking into the cell from the air. Some instruments measure the rate at which I_2 must be generated to maintain the end point and then compare this rate with that measured before sample was added. Other instruments allow you to set a "persistence of end point" time, typically 5 to 60 s, during which the detector voltage must be stable to define the end point.

A round robin study of accuracy and precision of the coulometric procedure identified sources of systematic error.[34] In some labs, either the instruments were inaccurate or workers did not measure the quantity of standards accurately. In other cases, the solvent was not appropriate. Commercial reagents are designed for Karl Fischer analysis. Reagents recommended by the instrument manufacturer should be used with each instrument.

Terms to Understand

amalgam
ampere
amperometry
auxiliary electrode
biosensor
bipotentiometric titration
charging current
Clark electrode
concentration polarization
controlled-potential electrolysis
coulomb
coulometric titration
coulometry
cyclic voltammetry
depolarizer
diffusion current
dropping-mercury electrode
electric double layer
electroactive species
electrogravimetric analysis
electrolysis
faradaic current
half-wave potential
Karl Fischer titration
mediator
ohmic potential
overpotential
nonpolarizable electrode
polarizable electrode
polarographic wave
polarography
potentiostat
reference electrode
residual current
rotating disk electrode
sampled current polarography
square wave voltammetry
stripping analysis
underpotential deposition
voltammetry
voltammogram
working electrode

Summary

In electrolysis, a chemical reaction is forced to occur by the flow of electricity through a cell. The moles of electrons flowing through the cell are It/F, where I is current, t is time, and F is the Faraday constant. The magnitude of the voltage that must be applied to an electrolysis cell is $E = E(\text{cathode}) - E(\text{anode}) - IR -$ overpotentials.

1. Overpotential is the voltage required to overcome the activation energy of an electrode reaction. A greater overpotential is required to drive a reaction at a faster rate.
2. Ohmic potential ($= IR$) is that voltage needed to overcome internal resistance of the cell.
3. Concentration polarization occurs when the concentration of electroactive species near an electrode is not the same as its concentration in bulk solution. Concentration polarization is embedded in the terms E(cathode) and E(anode).

Overpotential, ohmic potential, and concentration polarization always oppose the desired reaction and require a greater voltage to be applied for electrolysis.

Controlled-potential electrolysis is conducted in a three-electrode cell in which the potential of the working electrode is measured with respect to a reference electrode to which negligible current flows. Current flows between the working and auxiliary electrodes.

In electrogravimetric analysis, analyte is deposited on an electrode, whose increase in mass is then measured. With a constant voltage in a two-electrode cell, electrolysis is not very selective, because the working electrode potential changes as the reaction proceeds.

In coulometry, the moles of electrons needed for a chemical reaction are measured. In a coulometric (constant-current) titration, the time needed for complete reaction measures the number of electrons consumed. Controlled-potential coulometry is more selective than constant-current coulometry, but slower. Electrons consumed in the reaction are measured by integrating the current-versus-time curve.

In amperometry, current at the working electrode is proportional to analyte concentration. The amperometric glucose monitor generates H_2O_2 by enzymatic oxidation of glucose, and the H_2O_2 is measured by oxidation at an electrode. A mediator is employed to rapidly shuttle electrons between electrode and analyte. A coulometric glucose monitor counts electrons released by oxidation of all glucose in a small blood sample. "Electrical wiring" of the enzyme and mediator in a glucose monitor increases signal from the desired reaction and decreases background current from mediator diffusing to the auxiliary electrode.

Voltammetry is a collection of methods in which the dependence of current on the applied potential of the working electrode is observed. Polarography is voltammetry with a dropping-mercury working electrode. This electrode gives reproducible results because fresh surface is always exposed. Hg is useful for reductions because the high overpotential for H^+ reduction on Hg prevents interference by H^+ reduction. Oxidations are usually studied with other electrodes because Hg is readily oxidized. For quantitative analysis, the diffusion current is proportional to analyte concentration if there is a sufficient concentration of supporting electrolyte. The half-wave potential is characteristic of a particular analyte in a particular medium.

Sampled current polarography uses a staircase voltage profile for measurements with successive, static drops of Hg. One second after each voltage step, charging current is nearly 0, but there is still substantial faradaic current from the redox reaction.

Square wave polarography achieves increased sensitivity and a derivative peak shape by applying a square wave superimposed on a staircase voltage ramp. With each cathodic pulse, there is a rush of analyte to be reduced at the electrode surface. During the anodic pulse, reduced analyte is reoxidized. The polarogram is the difference between the cathodic and anodic currents. Square wave polarography permits fast, real-time measurements not possible with other electrochemical methods.

Stripping is the most sensitive form of voltammetry. In anodic stripping polarography, analyte is concentrated into a single drop or thin film of mercury by reduction at a fixed voltage for a fixed time. The potential is then made more positive, and current is measured as analyte is reoxidized. In cyclic voltammetry, a triangular waveform is applied, and cathodic and anodic processes are observed in succession. Microelectrodes fit into small places, and their low current allows them to be used in resistive, nonaqueous media. Their low capacitance increases sensitivity by reducing charging current and permits rapid voltage scanning, which allows very short-lived species to be studied.

The Karl Fischer titration of water uses a buret to deliver reagent or coulometry to generate reagent. In bipotentiometric end-point detection, the voltage needed to maintain a constant current between two Pt electrodes is measured. Voltage changes abruptly at the equivalence point, when one member of a redox couple is either created or destroyed.

Exercises

16-A. A dilute Na_2SO_4 solution is to be electrolyzed with a pair of smooth Pt electrodes at a current density of 100 A/m^2 and a current of 0.100 A. The products are $H_2(g)$ and $O_2(g)$ at 1.00 bar. Calculate the required voltage if the cell resistance is 2.00 Ω and there is no concentration polarization. What voltage would be required if the Pt electrodes were replaced by Au electrodes?

16-B. (a) At what cathode potential will Sb(s) deposition commence from 0.010 M SbO^+ solution at pH 0.00? Express this potential versus S.H.E. and versus Ag | AgCl.

$$SbO^+ + 2H^+ + 3e^- \rightleftharpoons Sb(s) + H_2O \qquad E^\circ = 0.208\ V$$

(b) What percentage of 0.10 M Cu^{2+} could be reduced electrolytically to Cu(s) before 0.010 M SbO^+ in the same solution begins to be reduced at pH 0.00?

16-C. Calculate the cathode potential (versus S.C.E.) needed to reduce cobalt(II) to 1.0 μM in each of the following solutions. In each case, Co(s) is the product of the reaction.

(a) 0.10 M $HClO_4$

(b) 0.10 M $C_2O_4^{2-}$ (Find the potential at which $[Co(C_2O_4)_2^{2-}] = 1.0\ \mu M$.)

$$Co(C_2O_4)_2^{2-} + 2e^- \rightleftharpoons Co(s) + 2C_2O_4^{2-} \qquad E^\circ = -0.474\ V$$

(c) 0.10 M EDTA at pH 7.00 (Find the potential at which $[Co(EDTA)^{2-}] = 1.0\ \mu M$.)

16-D. Ions that react with Ag^+ can be determined electrogravimetrically by deposition on a silver working anode:

$$Ag(s) + X^- \rightarrow AgX(s) + e^-$$

(a) What will be the final mass of a silver anode used to electrolyze 75.00 mL of 0.023 80 M KSCN if the initial mass of the anode is 12.463 8 g?

(b) At what electrolysis voltage (versus S.C.E.) will AgBr(s) be deposited from 0.10 M Br^-? (Consider negligible current flow, so that there is no ohmic potential, concentration polarization, or overpotential.)

(c) Is it theoretically possible to separate 99.99% of 0.10 M KI from 0.10 M KBr by controlled-potential electrolysis?

16-E. Chlorine has been used for decades to disinfect drinking water. An undesirable side effect of this treatment is reaction with organic impurities to create organochlorine compounds, some of which could be toxic. Monitoring total organic halide (designated TOX) is required for many water providers. A standard procedure for TOX is to pass water through activated charcoal, which adsorbs organic compounds. Then the charcoal is combusted to liberate hydrogen halides:

$$\text{Organic halide (RX)} \xrightarrow{O_2/800^\circ C} CO_2 + H_2O + HX$$

HX is absorbed into aqueous solution and measured by coulometric titration with a silver anode:

$$X^-(aq) + Ag(s) \rightarrow AgX(s) + e^-$$

When 1.00 L of drinking water was analyzed, a current of 4.23 mA was required for 387 s. A blank prepared by oxidizing charcoal required 6 s at 4.23 mA. Express the TOX of the drinking water as μmol halogen/L. If all halogen is chlorine, express the TOX as μg Cl/L.

16-F. Cd^{2+} was used as an internal standard in the analysis of Pb^{2+} by square wave polarography. Cd^{2+} gives a reduction wave at −0.60 (±0.02) V and Pb^{2+} gives a reduction wave at −0.40 (±0.02) V. It was first verified that the ratio of peak heights is proportional to the ratio of concentrations over the whole range employed in the experiment. Here are results for known and unknown mixtures.

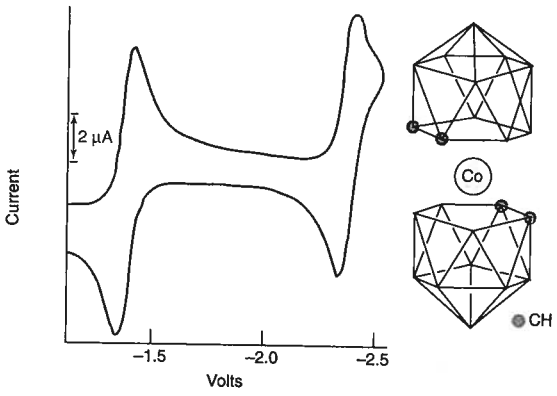
Analyte	Concentration (M)	Current (μA)
Known		
Cd^{2+}	$3.23\ (\pm0.01) \times 10^{-5}$	1.64 (±0.03)
Pb^{2+}	$4.18\ (\pm0.01) \times 10^{-5}$	1.58 (±0.03)
Unknown + Internal Standard		
Cd^{2+}	?	2.00 (±0.03)
Pb^{2+}	?	3.00 (±0.03)

The unknown mixture was prepared by mixing 25.00 (±0.05) mL of unknown (containing only Pb^{2+}) plus 10.00 (±0.05) mL of $3.23\ (\pm0.01) \times 10^{-4}$ M Cd^{2+} and diluting to 50.00 (±0.05) mL.

(a) Disregarding uncertainties, find $[Pb^{2+}]$ in the undiluted unknown.

(b) Find the absolute uncertainty for the answer to part (a).

16-G. Consider the cyclic voltammogram of the Co^{3+} compound $Co(B_9C_2H_{11})_2^-$. Suggest a chemical reaction to account for each wave. Are the reactions reversible? How many electrons are involved in each step? Sketch the sampled current and square wave polarograms expected for this compound.



Cyclic voltammogram of $Co(B_9C_2H_{11})_2^-$. [From W. E. Geiger, Jr., W. L. Bowden, and N. El Murr, "An Electrochemical Study of the Protonation Site of the Cobaltocene Anion and of Cyclopentadienylcobalt(I) Dicarbollides," *Inorg. Chem.* 1979, *18*, 2358.]

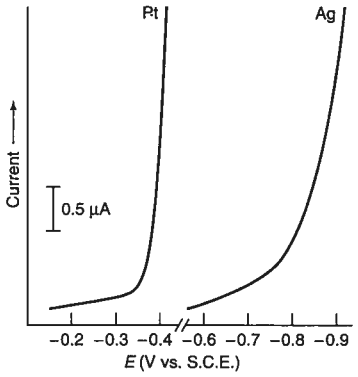
$E_{1/2}$ (V vs. S.C.E)	I_{pa}/I_{pc}	$E_{pa} - E_{pc}$ (mV)
−1.38	1.01	60
−2.38	1.00	60

16-H. In a coulometric Karl Fischer water analysis, 25.00 mL of pure "dry" methanol required 4.23 C to generate enough I_2 to react with the residual H_2O in the methanol. A suspension of 0.847 6 g of finely ground polymeric material in 25.00 mL of the same "dry" methanol required 63.16 C. Find the weight percent of H_2O in the polymer.

Problems

Fundamentals of Electrolysis

16-1. The figure shows the behavior of Pt and Ag cathodes at which reduction of H_3O^+ to $H_2(g)$ occurs. Explain why the two curves are not superimposed.



Current versus voltage for Pt and Ag electrodes in O_2-free, aqueous H_2SO_4 adjusted to pH 3.2. [From D. Marín, F. Mendicuti, and C. Teijeiro, "An Electrochemistry Experiment: Hydrogen Evolution Reaction on Different Electrodes," *J. Chem. Ed.* 1994, *71*, A277.]

16-2. How many hours are required for 0.100 mol of electrons to flow through a circuit if the current is 1.00 A?

16-3. The standard free energy change for the formation of $H_2(g) + \frac{1}{2}O_2(g)$ from $H_2O(l)$ is $\Delta G^\circ = +237.13$ kJ. The reactions are

Cathode: $2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$

Anode: $H_2O \rightleftharpoons \frac{1}{2}O_2(g) + 2H^+ + 2e^-$

Calculate the standard voltage (E°) needed to decompose water into its elements by electrolysis. What does the word *standard* mean in this question?

16-4. Consider the following electrolysis reactions.

Cathode: $H_2O(l) + e^- \rightleftharpoons \frac{1}{2}H_2(g, 1.0\text{ bar}) + OH^+(aq, 0.10\text{ M})$

Anode: $Br^-(aq, 0.10\text{ M}) \rightleftharpoons \frac{1}{2}Br_2(l) + e^-$

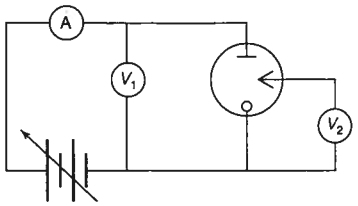
(a) Calculate the voltage needed to drive the net reaction if current is negligible.

(b) Suppose that the cell has a resistance of 2.0 Ω and a current of 100 mA. How much voltage is needed to overcome the cell resistance? This is the ohmic potential.

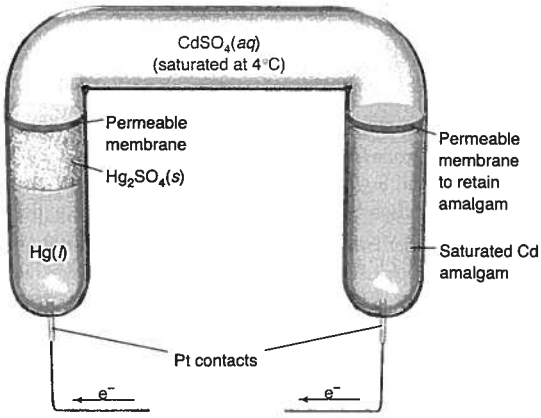
(c) Suppose that the anode reaction has an overpotential of 0.20 V and that the cathode overpotential is 0.40 V. What voltage is needed to overcome these effects combined with those of parts **(a)** and **(b)**?

(d) Suppose that concentration polarization occurs. $[OH^-]_s$ at the cathode surface increases to 1.0 M and $[Br^-]_s$ at the anode surface decreases to 0.010 M. What voltage is needed to overcome these effects combined with those of **(b)** and **(c)**?

16-5. Which voltage, V_1 or V_2, in the diagram (see top of next column), is constant in controlled-potential electrolysis? Which are the working, auxiliary, and reference electrodes in the diagram?



16-6. The Weston cell is a stable voltage standard formerly used in potentiometers. (The potentiometer compares an unknown voltage with that of the standard. In contrast with the conditions of this problem, very little current may be drawn from the cell if it is to be a voltage standard.)



$Hg_2SO_4 + Cd(in\ Hg) \rightleftharpoons 2Hg + CdSO_4$

(a) How much work (J) can be done by the Weston cell if the voltage is 1.02 V and 1.00 mL of Hg (density = 13.53 g/mL) is deposited?

(b) If the cell passes current through a 100-Ω resistor that dissipates heat at a rate of 0.209 J/min, how many grams of Cd are oxidized each hour? (This question is not meant to be consistent with part **(a)**. The voltage is no longer 1.02 volts.)

16-7. The chlor-alkali process,[35] in which seawater is electrolyzed to produce Cl_2 and NaOH, is the second most important commercial electrolysis, behind production of aluminum.

Anode: $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

Hg cathode: $Na^+ + H_2O + e^- \rightarrow NaOH + \frac{1}{2}H_2$

The Nafion membrane (page 384) used to separate the anode and cathode compartments resists chemical attack. Its anionic side chains permit conduction of Na^+, but not anions. The cathode compartment contains pure water, and the anode compartment contains seawater from which Ca^{2+} and Mg^{2+} have been removed. Explain how the membrane allows NaOH to be formed free of NaCl.

16-8. A lead-acid battery in a car has six cells in series, each delivering close to 2.0 V for a total of 12 V when the battery is discharging. Recharging requires ~2.4 V per cell, or ~14 V for the entire battery.[36] Explain these observations in terms of Equation 16-6.

Electrogravimetric Analysis

16-9. A 0.326 8-g unknown containing $Pb(CH_3CHOHCO_2)_2$ (lead lactate, FM 385.3) plus inert material was electrolyzed to produce 0.111 1 g of PbO_2 (FM 239.2). Was the PbO_2 deposited at the anode or at the cathode? Find the weight percent of lead lactate in the unknown.

16-10. A solution of Sn^{2+} is to be electrolyzed to reduce the Sn^{2+} to Sn(s). Calculate the cathode potential (versus S.H.E.) needed to reduce $[Sn^{2+}]$ to 1.0×10^{-8} M if no concentration polarization occurs. What would be the potential versus S.C.E. instead of S.H.E.? Would the potential be more positive or more negative if concentration polarization occurred?

16-11. What cathode potential (versus S.H.E.) is required to reduce 99.99% of Cd(II) from a solution containing 0.10 M Cd(II) in 1.0 M ammonia if there is negligible current? Consider the following reactions and assume that nearly all Cd(II) is in the form $Cd(NH_3)_4^{2+}$.

$$Cd^{2+} + 4NH_3 \rightleftharpoons Cd(NH_3)_4^{2+} \qquad \beta_4 = 3.6 \times 10^6$$
$$Cd^{2+} + 2e^- \rightleftharpoons Cd(s) \qquad E^\circ = -0.402\ V$$

16-12. *Electroplating efficiency.*[37] Nickel was electrolytically plated onto a carbon electrode from a bath containing 290 g/L $NiSO_4 \cdot 6H_2O$, 30 g/L $B(OH)_3$, and 8 g/L NaCl at -1.2 V vs. Ag | AgCl. The most important side reaction is reduction of H^+ to H_2. In one experiment, a carbon electrode weighing 0.477 5 g before deposition weighed 0.479 8 g after 8.082 C had passed through the circuit. What percentage of the current went into the reaction $Ni^{2+} + 2e^- \rightarrow Ni(s)$?

Coulometry

16-13. Explain how the amperometric end-point detector in Figure 16-8 operates.

16-14. What does a mediator do?

16-15. The sensitivity of a coulometer is governed by the delivery of its minimum current for its minimum time. Suppose that 5 mA can be delivered for 0.1 s.

(a) How many moles of electrons are delivered by 5 mA for 0.1 s?

(b) How many milliliters of a 0.01 M solution of a two-electron reducing agent are required to deliver the same number of electrons?

16-16. The experiment in Figure 16-8 required 5.32 mA for 964 s for complete reaction of a 5.00-mL aliquot of unknown cyclohexene solution.

(a) How many moles of electrons passed through the cell?

(b) How many moles of cyclohexene reacted?

(c) What was the molarity of cyclohexene in the unknown?

16-17. $H_2S(aq)$ can be analyzed by titration with coulometrically generated I_2.

$$H_2S + I_2 \rightarrow S(s) + 2H^+ + 2I^-$$

To 50.00 mL of sample were added 4 g of KI. Electrolysis required 812 s at 52.6 mA. Calculate the concentration of H_2S (μg/mL) in the sample.

16-18. Ti^{3+} is to be generated in 0.10 M $HClO_4$ solution for coulometric reduction of azobenzene.

$$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O \qquad E^\circ = 0.100\ V$$

$$4Ti^{3+} + C_6H_5N{=}NC_6H_5 + 4H_2O \rightarrow 2C_6H_5NH_2 + 4TiO^{2+} + 4H^+$$

Azobenzene — Aniline

At the counter electrode, water is oxidized, and O_2 is liberated at a pressure of 0.20 bar. Both electrodes are made of smooth Pt, and each has a total surface area of 1.00 cm^2. The rate of reduction of the azobenzene is 25.9 nmol/s, and the resistance of the solution between the generator electrodes is 52.4 Ω.

(a) Calculate the current density (A/m^2) at the electrode surface. Use Table 16-1 to estimate the overpotential for O_2 liberation.

(b) Calculate the cathode potential (versus S.H.E.) assuming that $[TiO^{2+}]_{surface} = [TiO^{2+}]_{bulk} = 0.050$ M and $[Ti^{3+}]_{surface} = 0.10$ M.

(c) Calculate the anode potential (versus S.H.E.).

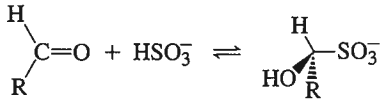
(d) What should the applied voltage be?

16-19. In an extremely accurate measurement of the Faraday constant, a pure silver anode was oxidized to Ag^+ with a constant current of 0.203 639 0 (±0.000 000 4) A for 18 000.075 (±0.010) s to give a mass loss of 4.097 900 (±0.000 003) g from the anode. Given that the atomic mass of Ag is 107.868 2 (±0.000 2), find the value of the Faraday constant and its uncertainty.

16-20. *Coulometric titration of sulfite in wine.*[38] Sulfur dioxide is added to many foods as a preservative. In aqueous solution, the following species are in equilibrium:

$$\underset{\text{Sulfur dioxide}}{SO_2} \rightleftharpoons \underset{\text{Sulfurous acid}}{H_2SO_3} \rightleftharpoons \underset{\text{Bisulfite}}{HSO_3^-} \rightleftharpoons \underset{\text{Sulfite}}{SO_3^{2-}} \qquad \text{(A)}$$

Bisulfite reacts with aldehydes in food near neutral pH:



Aldehyde — Adduct (B)

Sulfite is released from the adduct in 2 M NaOH and can be analyzed by its reaction with I_3^- to give I^- and sulfate. Excess I_3^- must be present for quantitative reaction.

Here is a coulometric procedure for analysis of total sulfite in white wine. Total sulfite means all species in Reaction A and the adduct in Reaction B. We use white wine so that we can see the color of a starch-iodine end point.

1. Mix 9.00 mL of wine plus 0.8 g NaOH and dilute to 10.00 mL. The NaOH releases sulfite from its organic adducts.
2. Generate I_3^- at the working electrode (the anode) by passing a known current for a known time through the cell in Figure 16-9. The cell contains 30 mL of 1 M acetate buffer (pH 3.7) plus 0.1 M KI. In the cathode compartment, H_2O is reduced to $H_2 + OH^-$. The frit retards diffusion of OH^- into the main compartment, where it would react with I_3^- to give IO^-.
3. Generate I_3^- at the anode with a current of 10.0 mA for 4.00 min.
4. Inject 2.000 mL of the wine/NaOH solution into the cell, where the sulfite reacts with I_3^-, leaving excess I_3^-.
5. Add 0.500 mL of 0.050 7 M thiosulfate to consume I_3^- by Reaction 15-19 and leave excess thiosulfate.
6. Add starch indicator to the cell and generate fresh I_3^- with a constant current of 10.0 mA. A time of 131 s was required to consume excess thiosulfate and reach the starch end point.

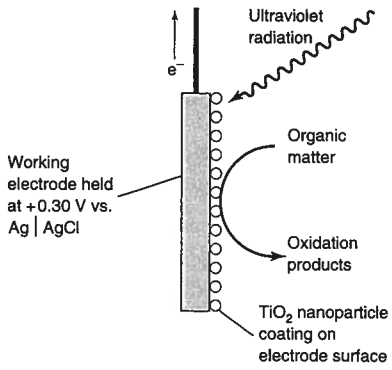
(a) In what pH range is each form of sulfurous acid predominant?

(b) Write balanced half-reactions for the anode and cathode.

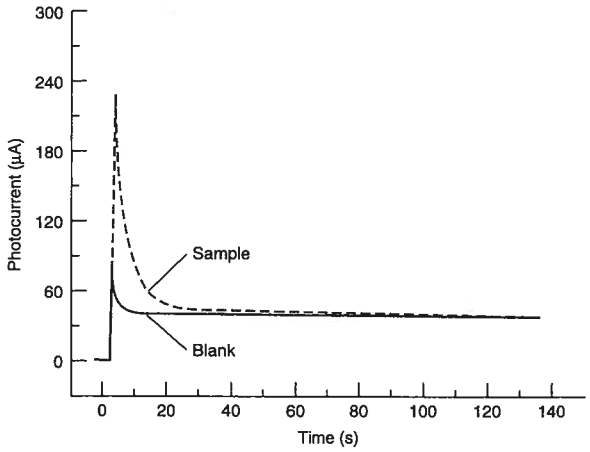
(c) At pH 3.7, the dominant form of sulfurous acid is HSO_3^- and the dominant form of sulfuric acid is HSO_4^{2-}. Write balanced reactions between I_3^- and HSO_3^- and between I_3^- and thiosulfate.

(d) Find the concentration of total sulfite in undiluted wine.

16-21. *Chemical oxygen demand by coulometry.* An electrochemical device incorporating photooxidation on a TiO_2 surface could replace refluxing with $Cr_2O_7^{2-}$ to measure chemical oxygen demand (Box 15-2). The diagram below shows a working electrode held at +0.30 V versus Ag | AgCl and coated with nanoparticles of TiO_2. Upon ultraviolet irradiation, electrons and holes are generated in the TiO_2. Holes oxidize organic matter at the surface. Electrons reduce H_2O at the auxiliary electrode in a compartment connected to the working compartment by a salt bridge. The sample compartment is only 0.18 mm thick with a volume of 13.5 μL. It requires ~1 min for all organic matter to diffuse to the TiO_2 surface and be exhaustively oxidized.



The blank curve in the graph below shows the response when the sample compartment contains just electrolyte. Before irradiation, no current is observed. Ultraviolet radiation causes a spike in the current, followed by a decrease to a steady level near 40 μA. This current arises from oxidation of water at the TiO_2 surface under ultraviolet exposure. The upper curve shows the same experiment, but with wastewater in the sample compartment. The increased current arises from oxidation of organic matter. When the organic matter is consumed, the current decreases to the blank level. The area between the two curves tells us how many electrons flow from oxidation of organic matter in the sample.



Photocurrent response for sample and blank. Both solutions contain 2 M $NaNO_3$. [From H. Zhao, D. Jiang, S. Zhang, K. Catterall, and R. John, "Development of a Direct Photoelectrochemical Method for Determination of Chemical Oxygen Demand," *Anal. Chem.* 2004, *76*, 155.]

(a) Balance the oxidation half-reaction that occurs in this cell:

$$C_cH_hO_oN_nX_x + AH_2O \rightarrow BCO_2 + CX^- + DNH_3 + EH^+ + Fe^-$$

where X is any halogen. Express the stoichiometry coefficients A, B, C, D, E, and F in terms of c, h, o, n, and x.

(b) How many molecules of O_2 are required to balance the half-reaction in part (a) by reduction of oxygen ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$)?

(c) The area between the two curves in the graph is $\int_0^\infty (I_{sample} - I_{blank})dt = 9.43$ mC. This is the number of electrons liberated by complete oxidation of the sample. How many moles of O_2 would be required for the same oxidation?

(d) Chemical oxygen demand (COD) is expressed as mg of O_2 required to oxidize 1 L of sample. Find the COD for this sample.

(e) If the only oxidizable substance in the sample were $C_9H_6NO_2ClBr_2$, what is its concentration in mol/L?

Amperometry

16-22. What is a Clark electrode, and how does it work?

16-23. (a) How does the amperometric glucose monitor in Figure 16-10 work?

(b) Why is a mediator advantageous in the glucose monitor?

(c) How does the coulometric glucose monitor in Figure 16-12 work?

(d) Why does the signal in the amperometric measurement depend on the temperature of the blood sample, whereas the signal in coulometry is independent of temperature? Do you expect the signal to increase or decrease with increasing temperature in amperometry?

(e) Glucose ($C_6H_6O_{12}$, FM 180.16) is present in normal human blood at a concentration near 1 g/L. How many microcoulombs are required for complete oxidation of glucose in 0.300 μL of blood in a home glucose monitor if the concentration is 1.00 g/L?

16-24. For a rotating disk electrode operating at sufficiently great potential, the redox reaction rate is governed by the rate at which analyte diffuses through the diffusion layer to the electrode (Figure 16-13b). The thickness of the diffusion layer is

$$\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2}$$

where D is the diffusion coefficient of reactant (m^2/s), ν is the kinematic viscosity of the liquid (= viscosity/density = m^2/s), and ω is the rotation rate (radians/s) of the electrode. There are 2π radians in a circle. The current density (A/m^2) is

$$\text{Current density} = 0.62 n F D^{2/3} \nu^{-1/6} \omega^{1/2} C_0$$

where n is the number of electrons in the half-reaction, F is the Faraday constant, and C_0 is the concentration of the electroactive species in bulk solution (mol/m^3, not mol/L). Consider the oxidation of $Fe(CN)_6^{4-}$ in a solution of 10.0 mM $K_3Fe(CN)_6$ + 50.0 mM $K_4Fe(CN)_6$ at +0.90 V (versus S.C.E.) at a rotation speed of 2.00×10^3 revolutions per minute.[20] The diffusion coefficient of $Fe(CN)_6^{4-}$ is 2.5×10^{-9} m^2/s, and the kinematic viscosity is 1.1×10^{-6} m^2/s. Calculate the thickness of the diffusion layer and the current density. If you are careful, the current density should look like the value in Figure 16-14b.

Voltammetry

16-25. In 1 M NH_3/1 M NH_4Cl solution, Cu^{2+} is reduced to Cu^+ near −0.3 (versus S.C.E.), and Cu^+ is reduced to Cu(*in Hg*) near −0.6 V.

(a) Sketch a qualitative sampled current polarogram for a solution of Cu^+.

(b) Sketch a polarogram for a solution of Cu^{2+}.

(c) Suppose that Pt, instead of Hg, were used as the working electrode. Which, if any, reduction potential would you expect to change?

16-26. (a) Explain the difference between charging current and faradaic current.

(b) What is the purpose of waiting 1 s after a voltage pulse before measuring current in sampled current voltammetry?

(c) Why is square wave voltammetry more sensitive than sampled current voltammetry?

16-27. Suppose that the diffusion current in a polarogram for reduction of Cd^{2+} at a mercury electrode is 14 μA. If the solution contains 25 mL of 0.50 mM Cd^{2+}, what percentage of Cd^{2+} is reduced in the 3.4 min required to scan from −0.6 to −1.2 V?

16-28. The drug Librium gives a polarographic wave with $E_{1/2}$ = −0.265 V (versus S.C.E.) in 0.05 M H_2SO_4. A 50.0-mL sample containing Librium gave a wave height of 0.37 μA. When 2.00 mL of 3.00 mM Librium in 0.05 M H_2SO_4 were added to the sample, the wave height increased to 0.80 μA. Find the molarity of Librium in the unknown.

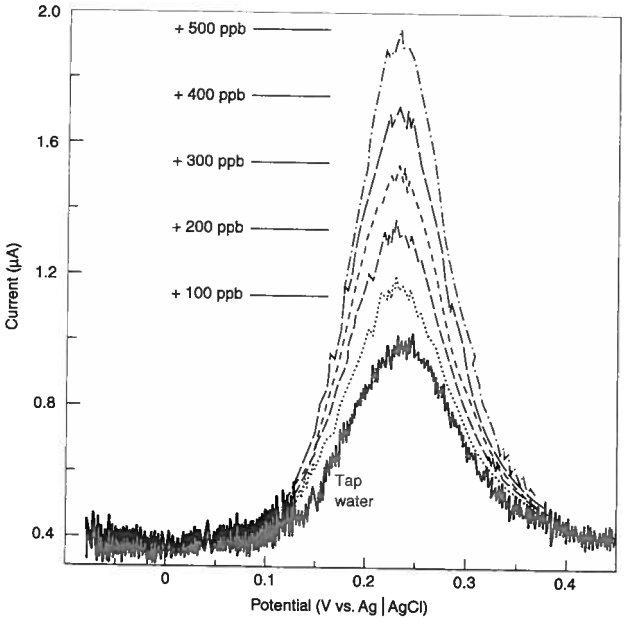
16-29. Explain what is done in anodic stripping voltammetry. Why is stripping the most sensitive voltammetric technique?

16-30. The figure below shows a series of standard additions of Cu^{2+} to acidified tap water measured by anodic stripping voltammetry at an iridium electrode. The unknown and all standard additions were made up to the same final volume.

(a) What chemical reaction occurs during the concentration stage of the analysis?

(b) What chemical reaction occurs during the stripping stage of the analysis?

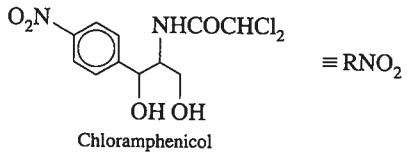
(c) Find the concentration of Cu^{2+} in the tap water.



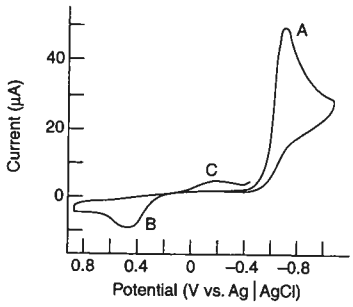
Anodic stripping voltammograms of tap water and five standard additions of 100 ppb Cu^{2+}. [From M. A. Nolan and S. P. Kounaves, "Microfabricated Array of Ir Microdisks for Determination of Cu^{2+} or Hg^{2+} Using Square Wave Stripping Voltammetry," *Anal. Chem.* 1999, *71*, 3567.]

16-31. From the two standard additions of 50 pm Fe(III) in Figure 16-23, find the concentration of Fe(III) in the seawater. Estimate where the baseline should be drawn for each trace and measure the peak height from the baseline. Consider the volume to be constant for all three solutions.

16-32. The cyclic voltammogram of the antibiotic chloramphenicol (abbreviated RNO_2) is shown here. The scan was started at 0 V, and potential was swept toward negative voltage. The first cathodic wave, A, is from the reaction $RNO_2 + 4e^- + 4H^+ \rightarrow RNHOH + H_2O$. Explain what happens at peaks B and C by using the reaction $RNO + 2e^- + 2H^+ \rightleftharpoons RNHOH$. Why was peak C not seen in the initial scan?

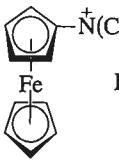


Chloramphenicol



Cyclic voltammogram of 3.7×10^{-4} chloramphenicol in 0.1 M acetate buffer, pH 4.62. The voltage of the carbon paste working electrode was scanned at a rate of 350 mV/s. [From P. T. Kissinger and W. R. Heineman, "Cyclic Voltammetry," *J. Chem. Ed.* 1983, *60*, 702.]

16-33. Peak current (I_p) and scan rate (ν) are listed for cyclic voltammetry (Fe(II) → Fe(III)) of a water-soluble ferrocene derivative in 0.1 M NaCl.[39]



Scan rate (V/s)	Peak anodic current (μA)
0.019 2	2.18
0.048 9	3.46
0.075 1	4.17
0.125	5.66
0.175	6.54
0.251	7.55

If a graph of I_p versus $\sqrt{\nu}$ gives a straight line, then the reaction is diffusion controlled. Prepare such a graph and use it to find the diffusion coefficient of the reactant for this one-electron oxidation. The area of the working electrode is 0.020 1 cm^2, and the concentration of reactant is 1.00 mM.

16-34. What are the advantages of using a microelectrode for voltammetric measurements?

16-35. What is the purpose of the Nafion membrane in Figure 16-30?

Karl Fischer Titration

16-36. Write the chemical reactions that show that 1 mol of I_2 is required for 1 mol of H_2O in a Karl Fischer titration.

16-37. Explain how the end point is detected in a Karl Fischer titration in Figure 16-32.

Quantitative Chemical Analysis

Eighth Edition

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