



## Chapter 37

# Voltammetric Techniques

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### Summary

#### General Uses

- Quantitative determination of organic and inorganic compounds in aqueous and nonaqueous solutions
- Measurement of kinetic rates and constants
- Determination adsorption processes on surfaces
- Determination electron transfer and reaction mechanisms
- Determination of thermodynamic properties of solvated species
- Fundamental studies of oxidation and reduction processes in various media
- Determination of complexation and coordination values

#### Common Applications

- Quantitative determination of pharmaceutical compounds
- Determination of metal ion concentrations in water to sub-parts-per-billion levels
- Determination of redox potentials
- Detection of eluted analytes in high-performance liquid chromatography (HPLC) and flow injection analysis

- Determination of number of electrons in redox reactions
- Kinetic studies of reactions

## Samples

### State

Species of interest must be dissolved in an appropriate liquid solvent and capable of being reduced or oxidized within the potential range of the technique and electrode material.

### Amount

The amounts needed to obtain appropriate concentrations vary greatly with the technique. For example, cyclic voltammetry generally requires analyte concentrations of  $10^{-3}$  to  $10^{-5}$  M, whereas anodic stripping voltammetry of metal ions gives good results with concentrations as low as  $10^{-12}$  M. Volumes may also vary from about 20 mL to less than a microliter (with special microelectrode cells).

### Preparation

The degree of preparation required depends on both the sample and the technique. For determination of Pb(II) and Cd(II) in seawater with a microelectrode and square-wave anodic stripping voltammetry (ASV), no preparation is required. In contrast, determination of epinephrine in blood plasma at a glassy carbon electrode with differential pulse voltammetry (DPV) requires that the sample first be pre-treated with several reagents, buffered, and separated.

## Analysis Time

Once the sample has been prepared, the time required to obtain a voltammogram varies from a few seconds using single-sweep square-wave voltammetry, to a couple of minutes for a cyclic voltammogram, to possibly 30 min (or more) for a very-low-concentration ASV determination.

## Limitations

### General

- Substance must be oxidizable or reducible in the range where the solvent and electrode are electrochemically inert.
- Provides very little or no information on species identity.
- Sample must be dissolved

### Accuracy

Accuracy varies with technique from 1 to 10%.

### Sensitivity and Detection Limits

Detection limit varies with technique from parts per thousand to parts per trillion.

## Complementary or Related Techniques

- Other electroanalytical techniques may provide additional or preliminary information for electrochemical properties.
- Simultaneous use of spectroscopic methods can identify species undergoing reaction.
- Liquid chromatography is often used to separate individual analytes before analysis.

## Introduction

Historically, the branch of electrochemistry we now call voltammetry developed from the discovery of polarography in 1922 by the Czech chemist Jaroslav Heyrovsky, for which he received the 1959 Nobel Prize in chemistry. The early voltammetric methods experienced a number of difficulties, making them less than ideal for routine analytical use. However, in the 1960s and 1970s significant advances were made in all areas of voltammetry (theory, methodology, and instrumentation), which enhanced the sensitivity and expanded the repertoire of analytical methods. The coincidence of these advances with the advent of low-cost operational amplifiers also facilitated the rapid commercial development of relatively inexpensive instrumentation.

The common characteristic of all voltammetric techniques is that they involve the application of a potential ( $E$ ) to an electrode and the monitoring of the resulting current ( $i$ ) flowing through the electrochemical cell. In many cases the applied potential is varied or the current is monitored over a period of time ( $t$ ). Thus, all voltammetric techniques can be described as some function of  $E$ ,  $i$ , and  $t$ . They are considered active techniques (as opposed to passive techniques such as potentiometry) because the applied potential forces a change in the concentration of an electroactive species at the electrode surface by electrochemically reducing or oxidizing it.

The analytical advantages of the various voltammetric techniques include excellent sensitivity with a very large useful linear concentration range for both inorganic and organic species ( $10^{-12}$  to  $10^{-1}$  M), a large number of useful solvents and electrolytes, a wide range of temperatures, rapid analysis times (seconds), simultaneous determination of several analytes, the ability to determine kinetic and mechanistic parameters, a well-developed theory and thus the ability to reasonably estimate the values of unknown parameters, and the ease with which different potential waveforms can be generated and small currents measured.

Analytical chemists routinely use voltammetric techniques for the quantitative determination of a variety of dissolved inorganic and organic substances. Inorganic, physical, and biological chemists widely use voltammetric techniques for a variety of purposes, including fundamental studies of oxidation and reduction processes in various media, adsorption processes on surfaces, electron transfer and reaction mechanisms, kinetics of electron transfer processes, and transport, speciation, and thermodynamic properties of solvated species. Voltammetric methods are also applied to the determination of compounds of pharmaceutical interest and, when coupled with HPLC, they are effective tools for the analysis of complex mixtures.

## How It Works

The electrochemical cell, where the voltammetric experiment is carried out, consists of a working (indicator) electrode, a reference electrode, and usually a counter (auxiliary) electrode. In general, an electrode provides the interface across which a charge can be transferred or its effects felt. Because the working electrode is where the reaction or transfer of interest is taking place, whenever we refer to the electrode, we always mean the working electrode. The reduction or oxidation of a substance at the surface of a working electrode, at the appropriate applied potential, results in the mass transport of new material to the electrode surface and the generation of a current. Even though the various types of voltammetric techniques may appear to be very different at first glance, their fundamental principles and applications derive from the same electrochemical theory. Here we summarize some of the electrochemical theory or laws common to all of the voltammetric techniques. Where necessary, more specific details are given later under the discussion of each technique.

## General Theory

In voltammetry, the effects of the applied potential and the behavior of the redox current are described by several well-known laws. The applied potential controls the concentrations of the redox species at the electrode surface ( $C_O^0$  and  $C_R^0$ ) and the rate of the reaction ( $k^0$ ), as described by the Nernst or Butler–Volmer equations, respectively. In the cases where diffusion plays a controlling part, the current resulting from the redox process (known as the faradaic current) is related to the material flux at the electrode–solution interface and is described by Fick’s law. The interplay between these processes is responsible for the characteristic features observed in the voltammograms of the various techniques.

For a reversible electrochemical reaction (that is, a reaction so fast that equilibrium is always reestablished as changes are made), which can be described by  $\mathbf{O} + ne^- \rightleftharpoons \mathbf{R}$ , the application of a potential  $E$  forces the respective concentrations of  $\mathbf{O}$  and  $\mathbf{R}$  at the surface of the electrode (that is,  $c_O^0$  and  $c_R^0$ ) to a ratio in compliance with the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{c_R^0}{c_O^0} \quad (37.1)$$

where  $R$  is the molar gas constant ( $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature ( $K$ ),  $n$  is the number of electrons transferred,  $F = \text{Faraday constant}$  ( $96,485 \text{ C/equiv}$ ), and  $E^0$  is the standard reduction potential for the redox couple. If the potential applied to the electrode is changed, the ratio  $c_R^0/c_O^0$  at the surface will also change so as to satisfy Eq. (37.1). If the potential is made more negative the ratio becomes larger (that is,  $\mathbf{O}$  is reduced) and, conversely, if the potential is made more positive the ratio becomes smaller (that is,  $\mathbf{R}$  is oxidized).

For some techniques it is useful to use the relationship that links the variables for current, potential, and concentration, known as the Butler–Volmer equation:

$$\frac{i}{nFA} = k^0 \{ c_O^0 \exp[-\alpha] - c_R^0 \exp[(1-\alpha)] \} \quad (37.2)$$

where  $\alpha = nF(E - E^0)/RT$ ,  $k^0$  is the heterogeneous rate constant,  $\alpha$  is known as the transfer coefficient, and  $A$  is the area of the electrode. This relationship allows us to obtain the values of the two analytically important parameters,  $i$  and  $k^0$ .

Finally, in most cases the current flow also depends directly on the flux of material to the electrode surface. When new  $\mathbf{O}$  or  $\mathbf{R}$  is created at the surface, the increased concentration provides the force for

its diffusion toward the bulk of the solution. Likewise, when **O** or **R** is destroyed, the decreased concentration promotes the diffusion of new material from the bulk solution. The resulting concentration gradient and mass transport is described by Fick's law, which states that the flux of matter ( ) is directly proportional to the concentration gradient:

$$= -AD_{\text{O}}(c_{\text{O}}/x) \quad (37.3)$$

where  $D_{\text{O}}$  is the diffusion coefficient of **O** and  $x$  is the distance from the electrode surface. An analogous equation can be written for **R**. The flux of **O** or **R** at the electrode surface controls the rate of reaction, and thus the faradaic current flowing in the cell. In the bulk solution, concentration gradients are generally small and ionic migration carries most of the current. The current is a quantitative measure of how fast a species is being reduced or oxidized at the electrode surface. The actual value of this current is affected by many additional factors, most importantly the concentration of the redox species, the size, shape, and material of the electrode, the solution resistance, the cell volume, and the number of electrons transferred.

In addition to diffusion, mass transport can also occur by migration or convection. Migration is the movement of a charged ion in the presence of an electric field. In voltammetry, the use of a supporting electrolyte at concentrations 100 times that of the species being determined eliminates the effect of migration. Convection is the movement of the electroactive species by thermal currents, by density gradients present in the solution, or by stirring the solution or rotating the electrode. Convection must be eliminated or controlled accurately to provide controlled transport of the analyte to the electrode.

Many voltammetric techniques have their own unique laws and theoretical relationships that describe and predict in greater detail the various aspects of the  $i$ - $E$  behavior (such as curve shape, peak height, width, and position). When appropriate, these are discussed in more detail.

## Instrumentation

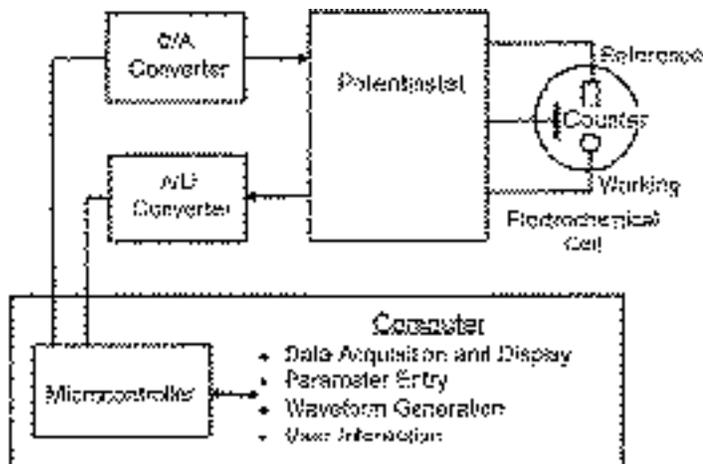
The basic components of a modern electroanalytical system for voltammetry are a potentiostat, computer, and the electrochemical cell (Fig. 37.1). In some cases the potentiostat and computer are bundled into one package, whereas in other systems the computer and the A/D and D/A converters and microcontroller are separate, and the potentiostat can operate independently.

### The Potentiostat

The task of applying a known potential and monitoring the current falls to the potentiostat. The most widely used potentiostats today are assembled from discrete integrated-circuit operational amplifiers and other digital modules. In many cases, especially in the larger instruments, the potentiostat package also includes electrometer circuits, A/D and D/A converters, and dedicated microprocessors with memory.

A simple potentiostat circuit for a three-electrode cell with three operational amplifiers (OA) is shown in Fig. 37.2. The output of OA-1 is connected to the counter electrode with feedback to its own inverting input through the reference electrode. This feedback decreases the difference between the inverting and noninverting inputs of OA-1 and causes the reference electrode to assume the same potential as  $E_{\text{in}}$  of OA-1. Because the potential difference between the working electrode and the reference electrode is zero the working electrode is set to the same potential as applied to the OA-1 input. With the reference electrode connected to  $E_{\text{in}}$  through the high impedance of OA-3, the current must flow through the counter electrode. Current flow through the reference not only is undesirable because of its higher resistance but also would eventually cause its potential to become unreliable. A three-electrode system is normally used in voltammetry for currents in the range of microamperes to

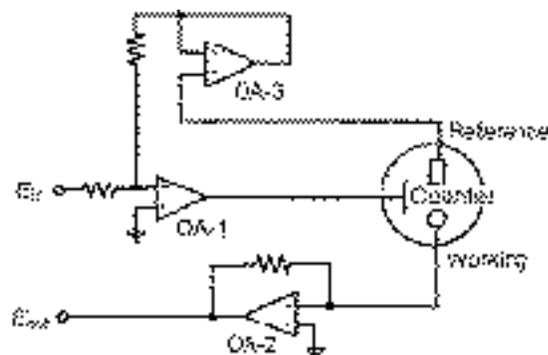
Figure 37.1 Block diagram of the major components of an electroanalytical system for performing voltammetric analysis.



milliamperes. With the use of micron-sized electrodes, currents are in the pico- to nanoampere range, and thus two electrodes are often used (that is, the counter and reference are tied together). An OA acting as a current-to-voltage converter (OA-2) provides the output signal for the A/D converter.

Most voltammetric techniques are dynamic (that is, they require a potential modulated according to some predefined waveform). Accurate and flexible control of the applied potential is a critical function of the potentiostat. In early analog instruments, a linear scan meant just that, a continuous linear change in potential from one preset value to another. Since the advent of digital electronics almost all potentiostats operate in a digital (incremental) fashion. Thus, the application of a linear scan is actually the application of a “staircase” modulated potential with small enough steps to be equivalent to the analog case. Not surprisingly, digital fabrication of the applied potential has opened up a whole new area of pulsed voltammetry, which gives fast experiments and increased sensitivity. In the simpler stand-

Figure 37.2 The basic potentiostat circuit composed of operational amplifiers.



one potentiostat the excitation signal used to modulate the applied potential is usually provided by an externally adjustable waveform generator. In the computer-controlled instruments, the properties of the modulation and the waveform are under software control and can be specified by the operator. The most commonly used waveforms are linear scan, differential pulse, and triangular and square wave.

The use of micro- and nanometer-size electrodes has made it necessary to build potentiostats with very low current capabilities. Microelectrodes routinely give current responses in the pico- to nanoampere range. High-speed scanning techniques such as square-wave voltammetry require very fast response times from the electronics. These diverse and exacting demands have pushed potentiostat manufacturers into providing a wide spectrum of potentiostats tailored to specific applications.

## The Electrodes and Cell

A typical electrochemical cell consists of the sample dissolved in a solvent, an ionic electrolyte, and three (or sometimes two) electrodes. Cells (that is, sample holders) come in a variety of sizes, shapes, and materials. The type used depends on the amount and type of sample, the technique, and the analytical data to be obtained. The material of the cell (glass, Teflon, polyethylene) is selected to minimize reaction with the sample. In most cases the reference electrode should be as close as possible to the working electrode; in some cases, to avoid contamination, it may be necessary to place the reference electrode in a separate compartment. The unique requirements for each of the voltammetric techniques are described under the individual techniques.

**Reference Electrodes** The reference electrode should provide a reversible half-reaction with Nernstian behavior, be constant over time, and be easy to assemble and maintain. The most commonly used reference electrodes for aqueous solutions are the calomel electrode, with potential determined by the reaction  $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- = 2\text{Hg}(\text{l}) + 2\text{Cl}^-$  and the silver/silver chloride electrode ( $\text{Ag}/\text{AgCl}$ ), with potential determined by the reaction  $\text{AgCl}(\text{s}) + \text{e}^- = \text{Ag}(\text{s}) + \text{Cl}^-$ . Table 37.1 shows the potentials of the commonly used calomel electrodes, along with those of some other reference electrodes. These electrodes are commercially available in a variety of sizes and shapes.

**Counter Electrodes** In most voltammetric techniques the analytical reactions at the electrode surfaces occur over very short time periods and rarely produce any appreciable changes in bulk concentrations of **R** or **O**. Thus, isolation of the counter electrode from the sample is not normally necessary. Most often the counter electrode consists of a thin Pt wire, although Au and sometimes graphite have also been used.

**Working Electrodes** The working electrodes are of various geometries and materials, ranging from small Hg drops to flat Pt disks. Mercury is useful because it displays a wide negative potential range (because it is difficult to reduce hydrogen ion or water at the mercury surface), its surface is readily regenerated by producing a new drop or film, and many metal ions can be reversibly reduced into it. Other commonly used electrode materials are gold, platinum, and glassy carbon.

**Table 37.1** Reference electrodes of the type || KCl/MCl(satd)/M.

MCl/M	KCl	$E^{\circ}$ at 25 °C	$\frac{d(E^{\circ})}{dt}$
		25	(mV/deg <sup>-1</sup> at 25 °C)
AgCl/Ag	3.5 M(at 25 °C)	0.205	-0.73
	Satd.	0.199	-1.01
Hg <sub>2</sub> Cl <sub>2</sub> /Hg	0.1 M(at 25 °C)	0.336	-0.08
	1.0 M(at 25 °C)	0.283	-0.29
	3.5 M(at 25 °C)	0.250	-0.39
	Satd.	0.244	-0.67

## What It Does

This section of the chapter discusses in more detail some of the more common forms of voltammetry currently in use for a variety of analytical purposes. The uniqueness of each rests on subtle differences in the manner and timing in which the potential is applied and the current measured. These differences can also provide very diverse chemical, electrochemical, and physical information, such as highly quantitative analyses, rate constants for chemical reactions, electrons involved on redox reactions, and diffusion constants.

## Polarography

Even though polarography could be considered just another variation of technique within voltammetry, it differs from other voltammetric methods both because of its unique place in the history of electrochemistry and in respect to its unique working electrode, the dropping mercury electrode (DME). The DME consists of a glass capillary through which mercury flows under gravity to form a succession of mercury drops. Each new drop provides a clean surface at which the redox process takes place, giving rise to a current increase with increasing area as the drop grows, and then falling when the drop falls. Figure 37.3 shows a polarogram for a 1 M solution of HCl that is 5 mM in Cd<sup>2+</sup>. The effect of drop growth and dislodging can be clearly seen. The potential when the current attains half the value of the plateau current is called the half-wave potential and is specific to the analyte's matrix. The plateau current is proportional to the concentration of analyte. For example, Fig. 37.4 shows a differential pulse polarogram for the acetyl derivative of chlordiazepoxide. In this case the peak height is proportional to the analyte concentration.

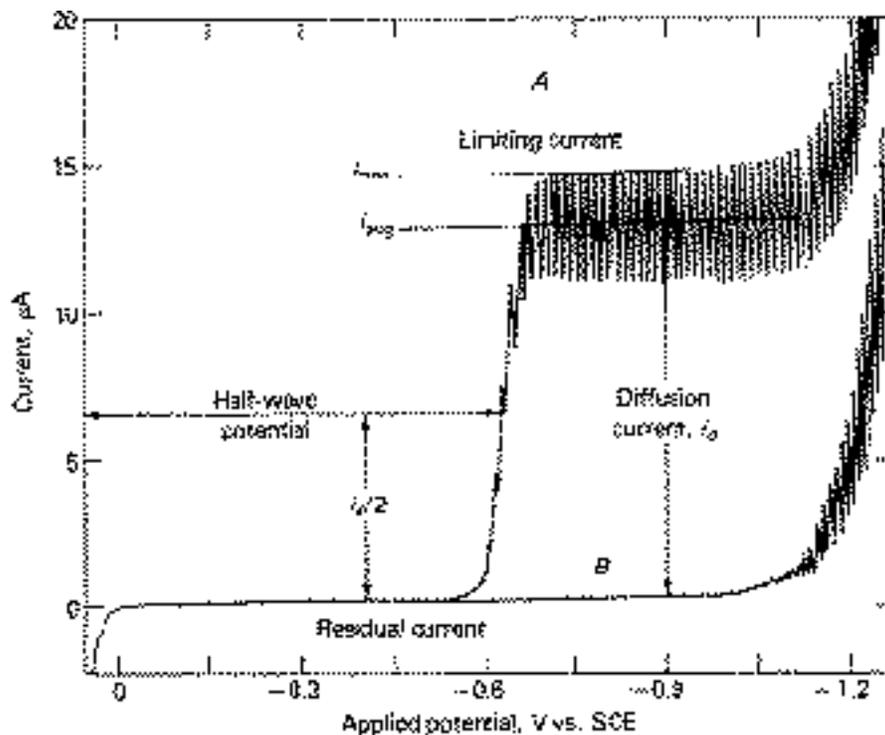
The current for the polarographic plateau can be predicted by the Ilkovic equation:

$$i_d = 708nD^{1/2}m^{2/3}t^{1/6}c^0 \quad (37.4)$$

where  $m$  is the rate of flow of the Hg through the capillary,  $t$  is the drop time, and  $c^0$  is the bulk analyte concentration.

Even though polarography with the DME is the best technique for some analytical determinations, it has several limitations. Mercury is oxidized at potentials more positive than +0.2 V versus SCE,

Figure 37.3 Classic polarogram taken at a DME showing background taken in 1 M HCl (line A) and 1 M HCl + 0.5 mM Cd(II) (line B). (From D. T. Sawyer and J. L. Roberts, *Experimental Electrochemistry for Chemists*, copyright © 1974 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)



which makes it impossible to analyze for any analytes in the positive region of potential. Another limitation is the residual current that results from charging of the large capacitance of the electrode surface.

By manipulating the potential and synchronizing potential pulses with current sampling, the same basic experiment can be made to yield a more useful result.

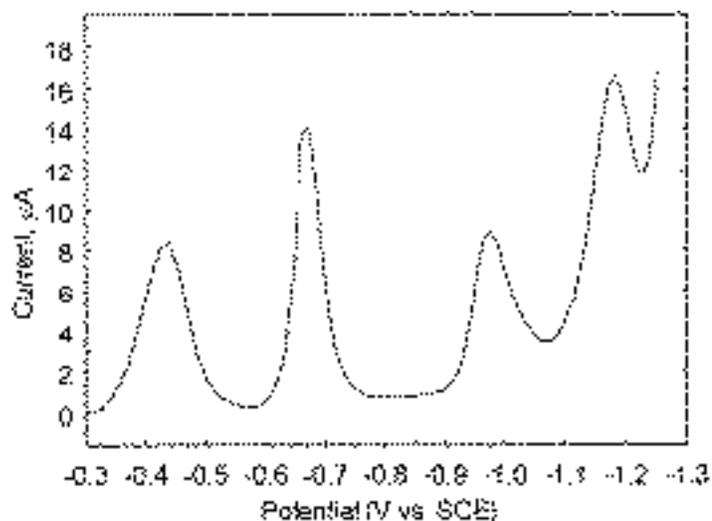
## Cyclic Voltammetry

Cyclic voltammetry (CV) has become an important and widely used electroanalytical technique in many areas of chemistry. It is rarely used for quantitative determinations, but it is widely used for the study of redox processes, for understanding reaction intermediates, and for obtaining stability of reaction products.

This technique is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential. At that point the scan would be reversed and run in the positive direction. Depending on the analysis, one full cycle, a partial cycle, or a series of cycles can be performed.

The response obtained from a CV can be very simple, as shown in Fig. 37.5 for the reversible redox system:

Figure 37.4 Differential pulse polarogram of the seven-acetyl analog of chlordiazepoxide. (Reprinted from *Anal. Chim. Acta*, 74, M. A. Brooks, et al., p. 367, copyright 1975 with kind permission of Elsevier Science—NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)



in which the complexed Fe(III) is reduced to Fe(II).

The important parameters in a cyclic voltammogram are the peak potentials ( $E_{pc}$ ,  $E_{pa}$ ) and peak currents ( $i_{pc}$ ,  $i_{pa}$ ) of the cathodic and anodic peaks, respectively. If the electron transfer process is fast compared with other processes (such as diffusion), the reaction is said to be electrochemically reversible, and the peak separation is

$$E_p = |E_{pa} - E_{pc}| = 2.303 RT/nF \quad (37.6)$$

Thus, for a reversible redox reaction at 25 °C with  $n$  electrons  $E_p$  should be 0.0592/ $n$  V or about 60 mV for one electron. In practice this value is difficult to attain because of such factors as cell resistance. Irreversibility due to a slow electron transfer rate results in  $E_p > 0.0592/n$  V, greater, say, than 70 mV for a one-electron reaction.

The formal reduction potential ( $E^o$ ) for a reversible couple is given by

$$E^o = \frac{E_{pc} + E_{pa}}{2} \quad (37.7)$$

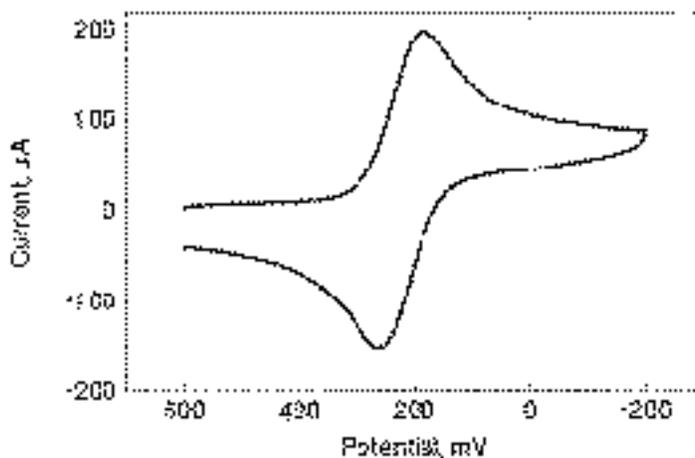
For a reversible reaction, the concentration is related to peak current by the Randles–Sevcik expression (at 25 °C):

$$i_p = 2.686 \times 10^5 n^{3/2} A c_0 D^{1/2} \nu^{1/2} \quad (37.8)$$

where  $i_p$  is the peak current in amps,  $A$  is the electrode area ( $\text{cm}^2$ ),  $D$  is the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ),  $c_0$  is the concentration in  $\text{mol cm}^{-3}$ , and  $\nu$  is the scan rate in  $\text{V s}^{-1}$ .

Cyclic voltammetry is carried out in quiescent solution to ensure diffusion control. A three-electrode arrangement is used. Mercury film electrodes are used because of their good negative potential range. Other working electrodes include glassy carbon, platinum, gold, graphite, and carbon paste.

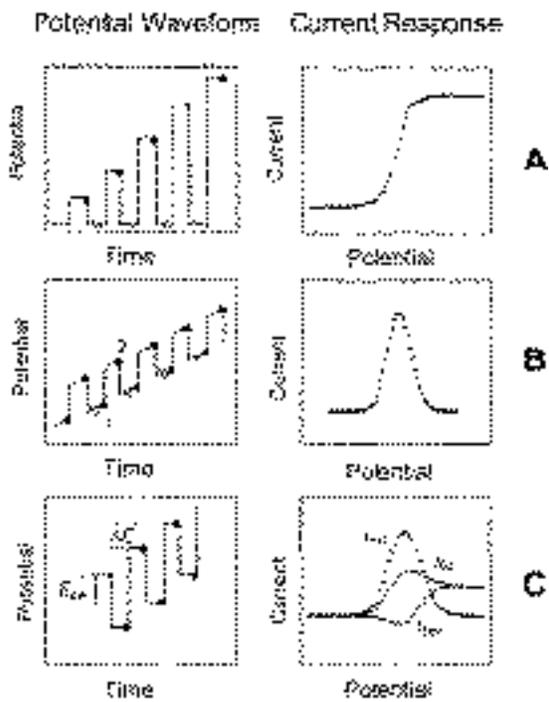
Figure 37.5 Cyclic voltammograms of 5 mM  $\text{Fe}(\text{CN})_6^{3-}$  in 1 M KCl with  $\nu = 500 \text{ mV/s}$ .



### Pulse Methods

In order to increase speed and sensitivity, many forms of potential modulation (other than just a simple staircase ramp) have been tried over the years. Three of these pulse techniques, shown in Fig. 37.6, are widely used.

Figure 37.6 Potential waveforms and their respective current response for (a) differential pulse, (b) normal pulse, and (c) square-wave voltammetry.



### Normal Pulse Voltammetry (NPV)

This technique uses a series of potential pulses of increasing amplitude. The current measurement is made near the end of each pulse, which allows time for the charging current to decay. It is usually carried out in an unstirred solution at either DME (called normal pulse polarography) or solid electrodes.

The potential is pulsed from an initial potential  $E_i$ . The duration of the pulse,  $t_p$ , is usually 1 to 100 msec and the interval between pulses typically 0.1 to 5 sec. The resulting voltammogram displays the sampled current on the vertical axis and the potential to which the pulse is stepped on the horizontal axis.

### Differential Pulse Voltammetry (DPV)

This technique is comparable to normal pulse voltammetry in that the potential is also scanned with a series of pulses. However, it differs from NPV because each potential pulse is fixed, of small amplitude (10 to 100 mV), and is superimposed on a slowly changing base potential. Current is measured at two points for each pulse, the first point (1) just before the application of the pulse and the second (2) at the end of the pulse. These sampling points are selected to allow for the decay of the nonfaradaic (charging) current. The difference between current measurements at these points for each pulse is determined and plotted against the base potential.

### Square-Wave Voltammetry (SWV)

The excitation signal in SWV consists of a symmetrical square-wave pulse of amplitude  $E_{sw}$  superimposed on a staircase waveform of step height  $E$ , where the forward pulse of the square wave coincides with the staircase step. The net current,  $i_{net}$ , is obtained by taking the difference between the forward and reverse currents ( $i_{for} - i_{rev}$ ) and is centered on the redox potential. The peak height is directly proportional to the concentration of the electroactive species and direct detection limits as low as  $10^{-8} M$  are possible.

Square-wave voltammetry has several advantages. Among these are its excellent sensitivity and the rejection of background currents. Another is the speed (for example, its ability to scan the voltage range over one drop during polarography with the DME). This speed, coupled with computer control and signal averaging, allows for experiments to be performed repetitively and increases the signal-to-noise ratio. Applications of square-wave voltammetry include the study of electrode kinetics with regard to preceding, following, or catalytic homogeneous chemical reactions, determination of some species at trace levels, and its use with electrochemical detection in HPLC.

## Preconcentration and Stripping Techniques

The preconcentration techniques have the lowest limits of detection of any of the commonly used electroanalytical techniques. Sample preparation is minimal and sensitivity and selectivity are excellent. The three most commonly used variations are anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), and adsorptive stripping voltammetry (AdSV).

Even though ASV, CSV, and AdSV each have their own unique features, all have two steps in common. First, the analyte species in the sample solution is concentrated onto or into a working electrode. It is this crucial preconcentration step that results in the exceptional sensitivity that can be achieved. During the second step, the preconcentrated analyte is measured or stripped from the electrode by the application of a potential scan. Any number of potential waveforms can be used for the

stripping step (that is, differential pulse, square wave, linear sweep, or staircase). The most common are differential pulse and square wave due to the discrimination against charging current. However, square wave has the added advantages of faster scan rate and increased sensitivity relative to differential pulse.

The electrode of choice for stripping voltammetry is generally mercury. The species of interest can be either reduced into the mercury, forming amalgams as in anodic stripping voltammetry, or adsorbed to form an insoluble mercury salt layer, as in cathodic stripping voltammetry.

Stripping voltammetry is a very sensitive technique for trace analysis. As with any quantitative technique, care must be taken so that reproducible results are obtainable. Important conditions that should be held constant include the electrode surface, rate of stirring, and deposition time. Every effort should be made to minimize contamination.

### Anodic Stripping Voltammetry

ASV is most widely used for trace metal determination and has a practical detection limit in the part-per-trillion range (Table 37.2). This low detection limit is coupled with the ability to determine simultaneously four to six trace metals using relatively inexpensive instrumentation.

Metal ions in the sample solution are concentrated into a mercury electrode during a given time period by application of a sufficient negative potential. These amalgamated metals are then stripped (oxidized) out of the mercury by scanning the applied potential in the positive direction. The resulting peak currents,  $i_p$ , are proportional to the concentration of each metal in the sample solution, with the position of the peak potential,  $E_p$ , specific to each metal. The use of mercury limits the working range for ASV to between approximately 0 and -1.2 V versus SCE. The use of thin Hg films or Hg micro-electrodes along with pulse techniques such as square-wave voltammetry can substantially lower the limits of detection of ASV.

With more than one metal ion in the sample, the ASV signal may sometimes be complicated by formation of intermetallic compounds, such as ZnCu. This may shift or distort the stripping peaks for the metals of interest. These problems can often be avoided by adjusting the deposition time or by changing the deposition potential.

### Cathodic Stripping Voltammetry

**Table 37.2** Relative sensitivity of some electrochemical techniques for metals.

Technique	Limits of Detection for Pb(II)
Ion selective electrode	$10^{-5}$ M
DC polarography at DME	$10^{-6}$ M
Differential pulse polarography at SMDE	$10^{-7}$ M
Differential pulse ASV at HMDE	$10^{-10}$ M*
DC ASV at mercury film	$10^{-11}$ M*
Square-wave ASV at mercury film	$10^{-12}$ M*

\*Deposition for 360 seconds; LOD varies with deposition time; SMDE = static (hanging) mercury drop electrode

CSV can be used to determine substances that form insoluble salts with the mercurous ion. Application of a relatively positive potential to a mercury electrode in a solution containing such substances results in the formation of an insoluble film on the surface of the mercury electrode. A potential scan in the negative direction will then reduce (strip) the deposited film into solution. This method has been used to determine inorganic anions such as halides, selenide, and sulfide, and oxyanions such as  $\text{MoO}_4^{2-}$  and  $\text{VO}_3^{5-}$ . In addition, many organic compounds, such as nucleic acid bases, also form insoluble mercury salts and may be determined by CSV.

### Adsorptive Stripping Voltammetry

AdSV is quite similar to anodic and cathodic stripping methods. The primary difference is that the pre-concentration step of the analyte is accomplished by adsorption on the electrode surface or by specific reactions at chemically modified electrodes rather than accumulation by electrolysis. Many organic species (such as heme, chlorpromazine, codeine, and cocaine) have been determined at micromolar and nanomolar concentration levels using AdSV; inorganic species have also been determined. The adsorbed species is quantified by using a voltammetric technique such as DPV or SWV in either the negative or positive direction to give a peak-shaped voltammetric response with amplitude proportional to concentration.

## Analytical Information

### Qualitative

As shown in Figs. 37.3 through 37.5, voltammetric techniques give rise to current signals that appear at a characteristic position on the potential scale. The potential at which the signal appears gives qualitative information about the reactant. However, the ability of the potential of the signal to identify the reactant is not very large because the position of the signal depends on the reactant conditions and the resolution is poor. Thus, a characteristic potential excludes many possibilities for the identity of the reactant; in particular, the voltammetric response absolutely excludes all nonelectroactive substances. If the response is the same as that of a known substance, obtained under exactly the same conditions, then the known substance is a good hypothesis for the identity. However, in general voltammetric techniques are not good tools for qualitative identification of analytes.

### Quantitative

The main virtue of voltammetric techniques is their good accuracy, excellent precision (<1%), sensitivity, and wide dynamic range. In the special case of stripping voltammetry, detection limits routinely are lower than the amount of signal due to contamination of sample. An impression of the relative ability of many electrochemical techniques to measure small concentrations of analytes in solution is given in Table 37.2. This table applies to routine practice with standard equipment. The detection limits given should be attainable, for example, in an undergraduate instructional laboratory.

## Nuts and Bolts

### Relative Costs

The size, power, sophistication, and price of the potentiostats for voltammetry vary from large research-grade instruments (20 to 30 kg with a  $\pm 10$ -volt potential and 1 A to 100 nA current ranges, \$15 to 20K) to simple battery-powered units (3 to 1 kg with a  $\pm 2.5$ -volt potential and 6 mA to 50 pA current ranges, \$3 to 8 K). The choice of instrument depends on the type of voltammetric analysis to be performed, the information desired, and somewhat on the size of the electrodes. Cyclic voltammetry experiments using 5-mm-diameter disk electrodes with scan rates no larger than  $1 \text{ V s}^{-1}$  are easily performed with most potentiostats. To determine quantitatively trace amounts of an analyte in an organic solvent using a 1- $\mu\text{m}$ -diameter microelectrode and high-frequency square-wave voltammetry requires the more expensive instrumentation. More detailed information is presented in Table 37.3.

### Vendors for Instruments and Accessories

In the United States there are several companies that manufacture electroanalytical instrumentation capable of performing voltammetric analyses and several who are distributors for U.S. or non-U.S. manufacturers. Table 37.3 lists the major vendors and a sample of the available models.

BioAnalytical Systems, Inc.

**Table 37.3** Manufacturers and distributors of voltammetric instrumentation.

Manufacturers/Distributors	Model	Techniques*	Price
BioAnalytical Systems, Inc.	CV27	Limited	\$3,995
	CV50W	Sufficient	11,500
	100BW	All	19,500
Cypress Systems, Inc.	OMN190	Limited	1,800
	CS1090	Sufficient	12,950
	CS2000	All	21,500
EG&G Princeton Applied Research	264	Limited	6,500
	263	All	11,440
	273A	All	18,695
Pine Instruments	AFRDE4	Limited	2,175
Brinkman Instruments (Metrohm)	693	Sufficient	18,670
Tacussell, France (ASL, Inc., U.S. distributor)	PJT	Sufficient	NA
Eco Chemie, Netherlands	PSTAT10	All	12,500

\*Limited = performs only a few techniques such as linear scan voltammetry; Sufficient = performs most of the common techniques; All = performs all or almost all of the major techniques.

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West Lafayette, IN 47906  
phone: 765-463-4527  
fax: 765-497-1102  
email: bas@bioanalytical.com  
Internet: <http://www.bioanalytical.com>

Cypress Systems, Inc.  
2500 West 31st St., Suite D  
Lawrence, KS 66047  
phone: 800-235-2436  
fax: 913-832-0406

EG&G Princeton Applied Research  
P.O. Box 2565  
Princeton, NJ 08543  
phone: 609-530-1000  
fax: 609-883-7259

Pine Instruments  
101 Industrial Dr.  
Grove City, PA 16127  
phone: 412-458-6391  
fax: 412-458-4648  
Internet: <http://www.pineinst.com>

Brinkman Instruments (Metrohm)  
One Cantiague Rd.  
P.O. Box 1019  
Westbury, NY 11590-0207  
phone: 800-645-3050  
fax: 516-334-7506  
email: info@brinkmann.com  
Internet: <http://www.brinkmann.com>

Eco Chemie B.V.  
P.O. Box 513  
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The Netherlands  
phone: +31 30 2893154  
fax: +31 30 2880715  
email: autolab@ecochemie.nl  
Internet: <http://www.ecochemie.nl>

## Required Level of Training

With modern commercial instrumentation, routine analytical voltammetry is made fairly straightforward by the manufacturer, who typically supplies not simply the instrument but rather a complete analytical system, including cell, electrodes, and software for data analysis. In cases for which the analyte is known and the method specified (often provided by the vendor), general training in chemistry at the postsecondary level is adequate. In less well-defined cases that involve some aspect of method devel-

opment, baccalaureate training and some specific experience with voltammetry are desirable. In the case of stripping methods, considerable experience with the specific techniques and problems of interest is often required, due not to increased complexity of the electrochemical technique but rather to general requirements for trace analysis involving sample handling, blank subtraction, and calibration.

## Service and Maintenance

Trouble with voltammetric procedures almost always arises in a part of the system external to the instrument. Thus, the first recourse when a problem arises is not to an electronics or software expert, but to someone with electrochemical experience. Most equipment manufacturers provide telephone consulting as well. Because of the integrated nature of the commercial equipment, repair of instruments is almost always done by returning the instrument to the factory. Typically no routine maintenance is required other than installation of software upgrades provided by the manufacturer. An instrument that functions well when first set up is most likely to do so for many years.

## Suggested Readings

- BAARS, A., M. SLUYTERS-REHBACH, AND J. H. SLUYTERS, "Application of the Dropping Mercury Microelectrode in Electrode Kinetics," *Journal of Electroanalytical Chemistry*, 364 (1994), 189.
- BARD, A. J. AND L. R. FAULKNER, *Electrochemical Methods*. New York: Wiley, 1980.
- BERSIER, B. M., "Do Polarography and Voltammetry Deserve Wider Recognition in Official and Recommended Methods?," *Analytical Proceedings*, 24 (1987), 44.
- BRETT, C. M. A., AND A. M. O. BRET, *Electrochemistry: Principles, Methods and Applications*. Oxford: Oxford University Press, 1993.
- CHRISTENSEN, P. A., AND A. HAMNET, *Techniques and Mechanisms in Electrochemistry*. New York: Chapman & Hall, 1994.
- GOSSER, D. K., *Cyclic Voltammetry: Simulation & Analysis of Reaction Mechanisms*. New York: VCH Publishers, 1993.
- KISSINGER, P. T., AND W. R. HEINEMAN, "Cyclic Voltammetry," *J. Chem. Ed.*, 60 (1983), 702.
- KISSINGER, P. T., AND W. R. HEINEMAN, *Laboratory Techniques in Electroanalytical Chemistry*. New York: Marcel Dekker, 1984.
- KOUNAVES, S. P., AND OTHERS, "Square Wave Anodic Stripping Voltammetry at the Mercury Film Electrode: Theoretical Treatment," *Analytical Chemistry*, 59 (1987), 386.
- O'DEA, J. J., J. OSTERYOUNG, AND R. A. OSTERYOUNG, "Theory of Square Wave Voltammetry for Kinetic Systems," *Analytical Chemistry*, 53 (1981), 695.
- OSTERYOUNG, J., AND R. A. OSTERYOUNG, "Square Wave Voltammetry," *Analytical Chemistry*, 57 (1985), 101A.
- RUDOLPH, M., D. P. REDDY, AND S. W. FELDBERG, "A Simulator for Cyclic Voltammetric Response," *Analytical Chemistry*, 66 (1994), 589A.
- VAN DEN BERG, C. M. G., "Potentials and Potentialities of Cathodic Stripping Voltammetry of Trace Elements in Natural Waters," *Anal. Chim. Acta*, 250 (1991), 265.
- WANG, J., *Stripping Analysis*. Deerfield Beach, FL: VCH Publishers, 1985.

