Cyclic Voltammetry

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Cyclic voltammetry (CV) is perhaps the most versatile electroanalytical technique for the study of electroactive species. Its versatility combined with ease of measurement has resulted in extensive use of CV in the fields of electrochemistry, inorganic chemistry, organic chemistry, and biochemistry. Cyclic voltammetry is often the first experiment performed in an electrochemical study of a compound, a biological material, or an electrode surface. The effectiveness of CV results from its capability for rapidly observing the redox behavior over a wide potential range. The resulting voltammogram is analogous to a conventional spectrum in that it conveys information as a function of an energy scan.

In spite of the wide usage enjoyed by CV, this technique is not generally well understood in comparison to other instrumental methods such as spectroscopy and chromatography. It is not uncommon for the experimenter who is performing CV to have a poor understanding of the basic concepts of the technique, such as why the voltammograms have their peculiar shapes. The brief treatment afforded CV in most instrumental analysis textbooks is insufficient to convey an in-depth understanding of this powerful technique.

It is the purpose of this article to provide a description of CV and its capabilities. The authors intend this to be suitable for a supplement to an undergraduate course in instrumental analysis or as an "initial reference" for anyone embarking on a CV experiment for the first time. This article is accompanied by an experiment which has been developed to demonstrate important features of CV.[1]

Fundamentals of Cyclic Voltammetry

CV consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of this *working electrode* is controlled versus a *reference electrode* such as a saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl). The controlling potential which is applied across these two electrodes can be considered an *excitation signal.* The excitation signal for CV is a linear potential scan with a triangular waveform as shown in Figure 1. This triangular potential excitation signal sweeps the potential of the electrode between two values, sometimes called the *switching potentials.* The excitation signal in Figure 1 causes the potential first to scan negatively from +0.80 to −0.20 V versus SCE at which point the scan direction is reversed, causing a positive scan back to the original potential of +0.80 V. The scan rate, as reflected by the slope, is 50 mV/s. A second cycle is indicated by the dashed line. Single or multiple cycles can be used. Modern instrumentation enables switching potentials and scan rates to be easily varied.

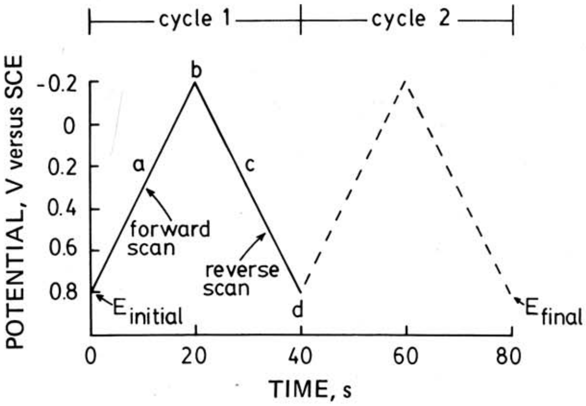

Figure 1. Typical excitation signal for cyclic voltammetry—a triangular potential waveform with switching potentials at 0.8 and −0.2 V versus SCE.

A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the *response signal* to the potential excitation signal. The voltammogram is a display of current (vertical axis) versus potential (horizontal axis). Because the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. This is helpful in understanding the fundamentals of the technique.

A typical cyclic voltammogram is shown in Figure 2 for a platinum working electrode in a solution containing 6.0 m*M* $K_3Fe(CN)_6$ as the electroactive species in 1.0 *M* KNO_3 in water as the supporting electrolyte. The potential excitation signal used to obtain this voltammogram is that shown in Figure 1, but with a negative switching potential of −0.15 V. Thus, the vertical axis in Figure 1 is now the horizontal axis for Figure 2. The *initial potential* (E_i) of 0.80 V applied at (a) is chosen to avoid any electrolysis of $Fe(CN)_6^{3-}$ when the electrode is switched on. The potential is then scanned *negatively, forward scan,* as indicated by the arrow. When the potential is sufficiently negative to reduce $Fe^{III}(CN)_6^{3-}$, *cathodic current* is indicated at (b) due to the electrode process

$$Fe^{III}(CN)_6^{3-} + e \rightarrow Fe^{II}(CN)_6^{4-} \qquad (1)$$

The electrode is now a sufficiently strong reductant to reduce $Fe^{III}(CN)_6^{3-}$. The cathodic current increases rapidly (b → d) until the concentration of $Fe^{III}(CN)_6^{3-}$ at the electrode surface is substantially diminished, causing the current to peak (d). The current then decays (d → g) as the solution surrounding

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[1] The experiment to accompany this article appears on page 772 of this issue.

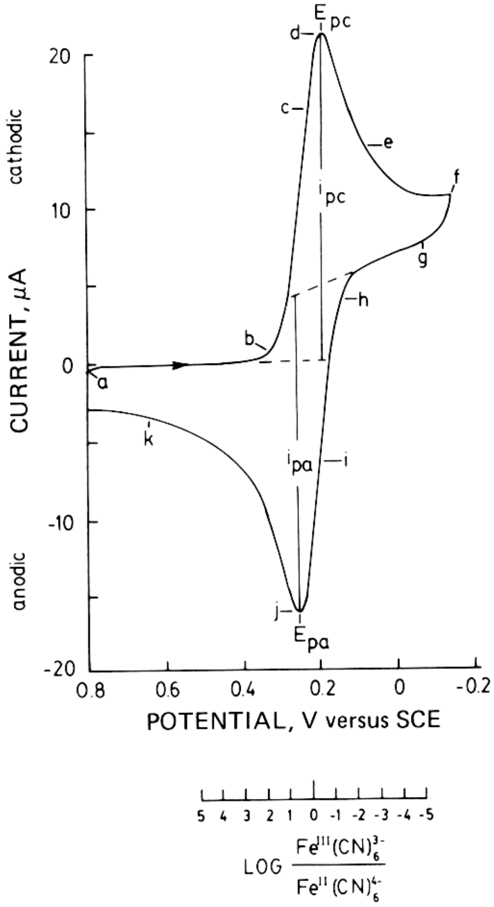


Figure 2. Cyclic voltammogram of 6 m*M* $K_3Fe(CN)_6$ in 1 *M* KNO_3. Scan initiated at 0.8 V versus SCE in negative direction at 50 mV/s. Platinum electrode, area = 2.54 mm^2.

the electrode is depleted of $Fe^{III}(CN)_6^{3-}$ due to its electrolytic conversion to $Fe^{II}(CN)_6^{4-}$. The scan direction is switched to *positive* at −0.15 V (f) for the *reverse scan.* The potential is still sufficiently negative to reduce $Fe^{III}(CN)_6^{3-}$, so cathodic current continues even though the potential is now scanning in the positive direction. When the electrode becomes a sufficiently strong oxidant, $Fe^{II}(CN)_6^{4-}$, which has been accumulating adjacent to the electrode, can now be oxidized by the electrode process

$$Fe^{II}(CN)_6^{4-} \rightarrow Fe^{III}(CN)_6^{3-} + e \qquad (2)$$

This causes *anodic current* (i → k). The anodic current rapidly increases until the surface concentration of $Fe^{II}(CN)_6^{4-}$ is diminished, causing the current to peak (j). The current then decays (j → k) as the solution surrounding the electrode is depleted of $Fe^{II}(CN)_6^{4-}$. The first cycle is completed when the potential reaches +0.80 V. Now that the cyclic voltammogram is obtained, it is apparent that any potential positive of ~ +0.4 V would be suitable as an initial potential in that reduction of $Fe^{III}(CN)_6^{3-}$ would not occur when the potential is applied. This procedure avoids inadvertent electrolysis as a result of applying the initial potential.

Simply stated, in the forward scan $Fe^{II}(CN)_6^{4-}$ is electrochemically generated from $Fe^{III}(CN)_6^{3-}$ as indicated by the cathodic current. In the reverse scan this $Fe^{II}(CN)_6^{4-}$ is oxidized back to $Fe^{III}(CN)_6^{3-}$ as indicated by the anodic current. Thus, CV is capable of rapidly generating a new oxidation state during the forward scan and then probing its fate on the reverse scan. This very important aspect of the technique will be illustrated in the section on coupled chemical reactions.

A more detailed understanding can be gained by considering the Nernst equation and the changes in concentration that occur in solution adjacent to the electrode during electrolysis. The potential excitation signal exerts control of the ratio of $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ at the electrode surface as described by the Nernst equation for a reversible system

$$E = E^{\circ\prime}_{Fe^{II}(CN)_6^{4-},Fe^{III}(CN)_6^{3-}} + \frac{0.059}{1}\log\frac{[Fe^{III}(CN)_6^{3-}]}{[Fe^{II}(CN)_6^{4-}]} \qquad (3)$$

where $E^{\circ\prime}$ is the formal reduction potential of the couple. An initial value of E which is sufficiently positive of $E^{\circ\prime}$ maintains a ratio in which $Fe^{III}(CN)_6^{3-}$ greatly predominates. Thus, application of +0.80 V as the initial potential causes negligible current. However, as E is scanned negatively, conversion of $Fe^{III}(CN)_6^{3-}$ to $Fe^{II}(CN)_6^{4-}$ by reduction is mandatory for satisfaction of the Nernst equation. The ratios of iron redox states that must exist at the *electrode surface* at several potentials during the scan are shown on the lower horizontal axis in Figure 2. The logarithmic relationship between E and $[Fe^{III}(CN)_6^{3-}]/[Fe^{II}(CN)_6^{4-}]$ is reflected by a rapid rate of change in the region where $E = E^{\circ\prime}$, i.e., $[Fe^{III}(CN)_6^{3-}]/[Fe^{II}(CN)_6^{4-}] = 1$. This causes the dramatic rise in cathodic current (b → d) during the forward scan.

The physical situation in the solution adjacent to the electrode during the potential scan is illustrated by the *concentration-distance profiles* (*C-x* profiles) in Figure 3 for selected potentials from Figure 2. A *C-x* profile is a graphical illustration of how solution concentration (C) varies as a function of distance (x) from the electrode surface.

The *C-x* profiles in Figure 3a are for $Fe^{III}(CN)_6^{3-}$ and $Fe^{II}(CN)_6^{4-}$ at the initial potential. Note that the application of E_i does not measurably alter the concentration of $Fe^{III}(CN)_6^{3-}$ at the electrode surface as compared to the solution bulk. As the potential is scanned negatively, the concentration of $Fe^{III}(CN)_6^{3-}$ at the electrode surface decreases in order to establish an $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ ratio which satisfies the Nernst equation for the applied potential at any particular instant. This is illustrated by profiles c–e. Note that profile (c) (for which the concentration of $Fe^{III}(CN)_6^{3-}$ at the electrode surface exactly equals the concentration of $Fe^{II}(CN)_6^{4-}$ corresponds to an E which equals the formal electrode potential (versus SCE) of the couple.

Profiles (e, g) correspond to potentials sufficiently negative of the formal electrode potential that the concentration of $Fe^{III}(CN)_6^{3-}$ is *effectively* zero at the electrode surface. The conditions for these profiles are analogous to those for chronoamperometry (*1*, *2*). Once the potential has reached a value sufficient for a zero reactant-surface-concentration, the potential and its rate of change become immaterial to the diffusion-controlled current. In other words, should the scan be stopped at (e), the current will follow the same time course as if the scan had been continued.

The behavior of the current during the potential scan can be understood by carefully examining the *C-x* profiles in Figure 3. The current is proportional to the slope of the *C-x* profile at the electrode surface as described by

$$i = nFAD\left(\frac{\partial C}{\partial x}\right)_{x=0} = K\left(\frac{\partial C}{\partial x}\right)_{x=0} \qquad (4)$$

where i is current (A), n is number of electrons transferred per ion (equivalents/mol), A is electrode area (cm^2), D is diffusion coefficient (cm^2/s), C is concentration (mol/cm^3), and x is distance from the electrode (cm). Thus, the current observed at a particular potential for the voltammogram in Figure 2 can be explained by the slope of the corresponding *C-x* profile in Figure 3. The slope of profile (a) is zero and current is negligible at that potential. As the potential is then scanned negatively, $(\partial C/\partial x)_{x=0}$ increases for profiles (c–d), and the cathodic current in Figure 2 increases correspondingly. However, when profile (d) is reached, $(\partial C/\partial x)_{x=0}$ decreases as shown by profiles (e) and (g) because of depletion of $Fe^{III}(CN)_6^{3-}$ near the electrode. Correspondingly, the current now drops. Thus, the observed current behavior for the voltammogram is an

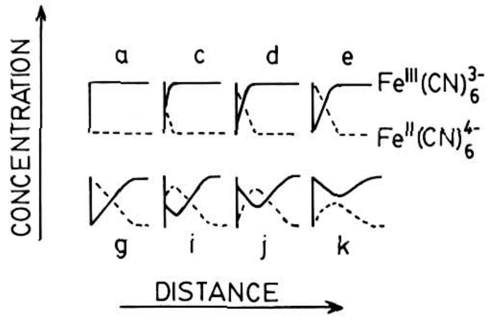


Figure 3. Concentration-distance (C-x) profiles for cyclic voltammogram in Figure 2.

increase to a peak current at which point the current decays due to depletion of electroactive species near the electrode.

During the negative scan in which $Fe^{III}(CN)_6{}^{3-}$ is reduced to $Fe^{II}(CN)_6{}^{4-}$, the depletion of $Fe^{III}(CN)_6{}^{3-}$ in the vicinity of the electrode is accompanied by an accumulation of $Fe^{II}(CN)_6{}^{4-}$. This can be seen by the C-x profiles for $Fe^{II}(CN)_6{}^{4-}$. After the direction of potential scan is switched at −0.15 V to a positive scan, reduction continues (as is evident by the cathodic current and the C-x profile) until the applied potential becomes sufficiently positive to cause oxidation of the accumulated $Fe^{II}(CN)_6{}^{4-}$. Oxidation of $Fe^{II}(CN)_6{}^{4-}$ is signaled by the appearance of anodic current. Once again, the current increases as the potential moves increasingly positive until the concentration of $Fe^{II}(CN)_6{}^{4-}$ becomes depleted at the electrode. At this point the current peaks and then begins to decrease. Thus, the physical phenomena which caused a current peak during the reduction cycle also cause a current peak during the oxidation cycle. This can be seen by comparing the C-x profiles for the two scans.

The important parameters of a cyclic voltammogram are the magnitudes of the *anodic peak current* (i_{pa}) and *cathodic peak current* (i_{pc}), and the *anodic peak potential* (E_{pa}) and *cathodic peak potential* (E_{pc}). These parameters are labeled in Figure 2. One method for measuring i_p involves extrapolation of a baseline current as shown in the figure. The establishment of a correct baseline is essential for the accurate measurement of peak currents. This is not always easy, particularly for more complicated systems.

A redox couple in which both species rapidly exchange electrons with the working electrode is termed an *electrochemically reversible* couple. The *formal reduction potential* ($E°'$) for a reversible couple is centered between E_{pa} and E_{pc}.

$$E^{\circ\prime} = \frac{E_{pa} + E_{pc}}{2} \tag{5}$$

The number of electrons transferred in the electrode reaction (n) for a reversible couple can be determined from the separation between the peak potentials

$$\Delta E_p = E_{pa} - E_{pc} \cong \frac{0.059}{n} \tag{6}$$

Thus, a one-electron process such as the reduction of $Fe^{III}(CN)_6{}^{3-}$ to $Fe^{II}(CN)_6{}^{4-}$ exhibits a ΔE_p of 0.059 V. Slow electron transfer at the electrode surface, "irreversibility," causes the peak separation to increase.

The peak current for a reversible system is described by the Randles-Sevcik equation for the forward sweep of the first cycle (*1, 2*)

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C \nu^{1/2} \tag{7}$$

where i_p is peak current (A), n is electron stoichiometry, A is electrode area (cm^2), D is diffusion coefficient (cm^2/s), C is concentration (mol/cm^3), and ν is scan rate (V/s). Accordingly, i_p increases with $\nu^{1/2}$ and is directly proportional to concentration. The relationship to concentration is particularly important in analytical applications and in studies of electrode mechanisms. The values of i_{pa} and i_{pc} should be identical for a simple reversible (fast) couple. That is

$$\frac{i_{pa}}{i_{pc}} = 1 \tag{8}$$

However, the ratio of peak currents can be significantly influenced by chemical reactions coupled to the electrode process, as discussed below.

Electrochemical irreversibility is caused by slow electron exchange of the redox species with the working electrode. In this case eqns. (5), (6), (7), and (8) are not applicable. Electrochemical irreversibility is characterized by a separation of peak potentials greater than indicated by eqn. (6) (*1, 3*).

Effect of Coupled Chemical Reactions

There are inorganic ions, metal complexes, and a few organic compounds which undergo electron transfer reactions without the making or breaking of covalent bonds. The vast majority of electrochemical reactions involve an electron transfer step which leads to a species which rapidly reacts with components of the medium via so-called coupled chemical reactions. One of the most useful aspects of CV is its application to the qualitative diagnosis of these homogeneous chemical reactions that are coupled to the electrode surface reaction (*1, 4–7*). CV provides the capability for generating a species during the forward scan and then probing its fate with the reverse scan and subsequent cycles, all in a matter of seconds or less. In addition, the time scale of the experiment is adjustable over several orders of magnitude by changing the potential scan rate, enabling some assessment of the rates of various reactions.

A detailed review of this aspect of CV cannot be accommodated in this brief article. We have chosen two examples which illustrate the chemistry associated with reducing an aromatic nitro compound in a weak acid buffer and oxidizing an aromatic ether in aqueous media of low pH. Both examples illustrate reactions which are paralleled by many hundreds of compounds readily available for use in undergraduate laboratories. Both involve the use of very inexpensive electrodes and convenient media. It should be noted that a great deal of modern electrochemistry is carried out using highly purified nonaqueous solvents which can be quite costly (and often toxic) and are not recommended for the beginner.

A cyclic voltammogram for the popular antibiotic chloramphenicol is illustrated in Figure 4. The scan was started in a negative direction from 0.0 volts. Three peaks are observed, peak A for the initial reduction, peak B for oxidation of a product of this reduction, and peak C for reduction of the product resulting from the events accounting for peak B. All three "peaks" or "waves" involve more than a simple electron transfer reaction.

peak A

$$R\phi NO_2 + 4e + 4H^+ \rightarrow R\phi NHOH + H_2O$$

peak B

$$R\phi NHOH \rightarrow R\phi NO + 2H^+ + 2e$$

peak C

$$R\phi NO + 2e + 2H^+ \rightarrow R\phi NHOH$$

To assist in "proving" the diagnosis, authentic samples of the hydroxylamine and nitroso derivative can be used to confirm the assignment of peak B and C.

Thyronine is an ether which may conveniently be thought of as representing the combination of the amino acid tyrosine

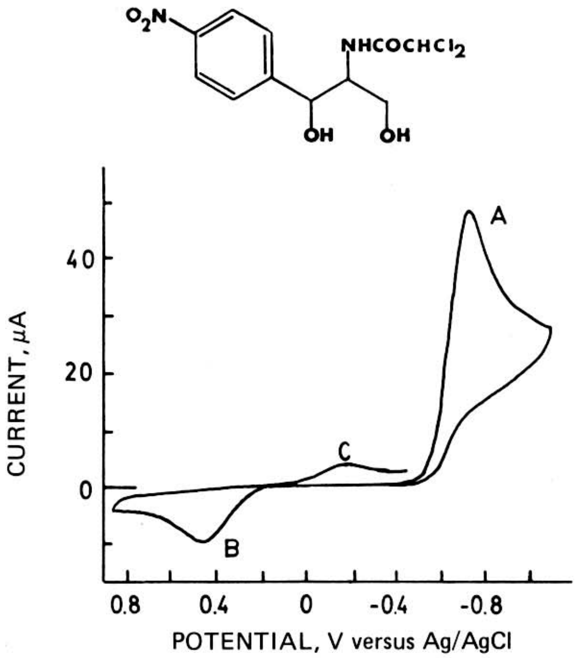
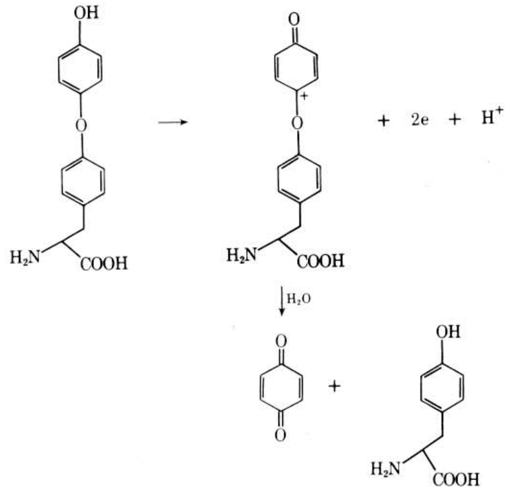


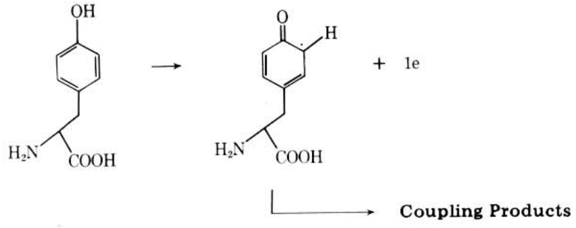
Figure 4. Cyclic voltammogram of 3.3 mg/25 ml chloramphenicol in 0.1 *M* acetate buffer, pH 4.62. Carbon paste electrode. Scan rate = 350 mV/s.

with hydroquinone. Its oxidative CV on a carbon paste electrode is illustrated in Figure 5. In this case the scan is initiated in a positive direction from 0.0 volts. The initial two-electron oxidation (peak A) generates a proton and an organic cation which is readily hydrolyzed to benzoquinone and tyrosine.



Peak A

The tyrosine thus produced is subsequently oxidized at peak B (no product from peak B is detected on the reverse scan).



Peak B

The benzoquinone is reduced on the reverse scan at peak C to produce hydroquinone,

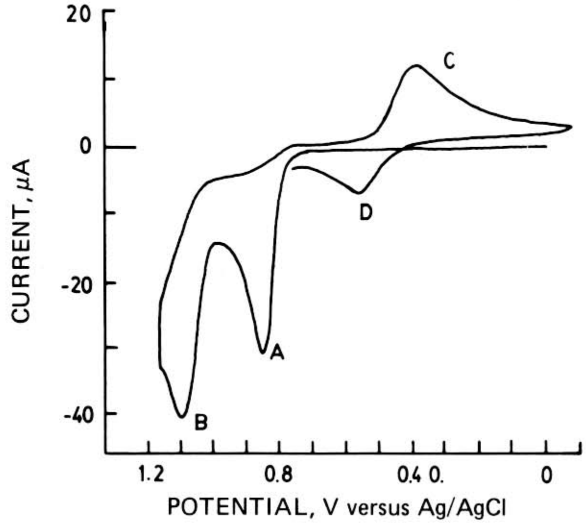
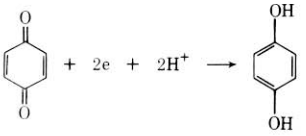
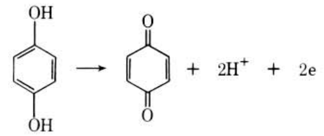


Figure 5. Cyclic voltammogram of 5 mg/25 ml L-thyronine in 1 *M* H_2SO_4. Carbon paste electrode, scan rate = 200 mV/s.



Peak C

which is then oxidized back to benzoquinone at peak D on the second positive-going half-cycle.



Peak D

Standard solutions of benzoquinone, hydroquinone, and tyrosine can be used to verify these assignments.

Interpreting complex cyclic voltammograms is often a challenge best met by the combination of chemical intuition with the study of model compounds, exactly in the same manner used by many spectroscopists to interpret optical, magnetic resonance, or mass spectra.

Instrumentation

Cyclic voltammetry requires a waveform generator to produce the excitation signal, a potentiostat to apply this signal to an electrochemical cell, a current-to-voltage converter to measure the resulting current, and an *XY* recorder or oscilloscope to display the voltammogram. The first three items are normally incorporated into a single electronic device although modular instruments are also used. The potentiostat insures that the working electrode potential will not be influenced by the reaction(s) which takes place. The functioning of potentiostats has been described elsewhere (*2*). Data are typically obtained via *XY* recorder at slow scans, i.e., less than

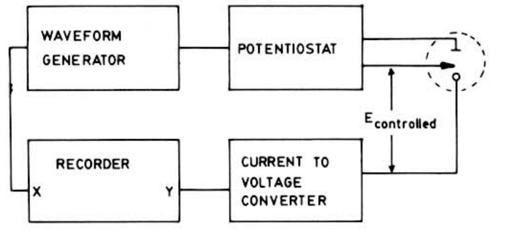


Figure 6. Instrumentation for cyclic voltammetry. Electrode designation: O— working, |— auxiliary, ← reference.

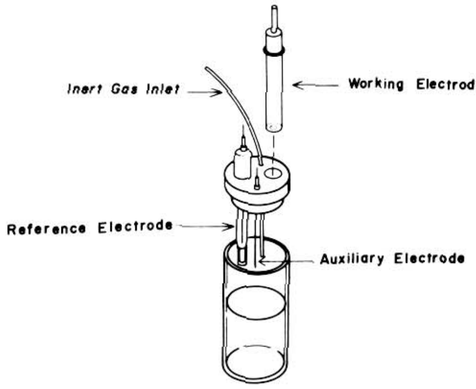


Figure 7. Electrochemical cell for voltammetry.

500 mV/s, and storage oscilloscope at faster rates. Scan rates up to 20,000 V/s have been used, however, rates faster than 100 V/s are rarely practical because of iR drop and charging current.

Modern potentiostats utilize a three-electrode configuration as shown in Figure 6. The potentiostat applies the desired potential between a working electrode and a reference electrode. The working electrode is the electrode at which the electrolysis of interest takes place. The current required to sustain the electrolysis at the working electrode is provided by the auxiliary electrode. This arrangement prevents large currents from passing through the reference electrode that could change its potential.

A typical electrochemical cell is illustrated in Figure 7. Such a cell usually consists of a glass container with a cap having holes for introducing electrodes and nitrogen. Provision is made for oxygen removal from solution by bubbling with nitrogen gas. The cell is then maintained oxygen free by passing nitrogen over the solution. The reference electrode is typically a SCE or a Ag/AgCl electrode which often is isolated from the solution by a salt bridge to prevent contamination by leakage from the reference electrode. The auxiliary electrode is usually a platinum wire that is placed directly into the solution. Since the limiting (or peak) current in any type of voltammetry is temperature-dependent, the cell should be thermostated for the most exacting work. For most purposes, however, this is not necessary. Cells are commercially available which require as little as 1–2 ml of solution. Thin-layer cells enable voltammograms to be recorded on down to 60 μL (*8*).

A large variety of working electrodes has been used with voltammetry. The voltammetric techniques termed *polarography* utilize the *dropping mercury electrode* (DME). This electrode consists of mercury drops continuously extruding from the end of a capillary. The *hanging mercury drop electrode* (HMDE) is commonly used for CV. Here a drop of mercury is suspended at the end of a capillary. A thin coat of mercury can be deposited on a substrate such as graphite to form a *mercury film electrode* (MFE). A significant advantage of mercury is its good negative potential range. Solid electrodes such as platinum, gold, glassy carbon, wax impregnated graphite, and carbon paste are also commonly used in CV. Such electrodes have a better positive potential range than mercury.

Conclusions

CV has become increasingly popular in all fields of chemistry as a means of studying redox states. The method enables a wide potential range to be scanned rapidly for reducible or oxidizable species. This capability together with its variable time scale and good sensitivity make this the most versatile electroanalytical technique thus far developed. It must, however, be emphasized that its merits are largely in the realm of qualitative or "diagnostic" experiments. Quantitatve measurements (of rates or concentrations) are *best* obtained via other means (e.g., "step" or "pulse" techniques). Because of the kinetic control of many CV experiments, some caution is advisable when evaluating the results in terms of thermodynamic parameters, e.g., measurement of $E^{\circ\prime}$.

Perhaps the most useful aspect of CV is its application to the qualitative diagnosis of electrode reactions which are coupled to homogeneous chemical reactions. The forte of CV is its ability to generate a species during one scan and then probe its fate with subsequent scans.

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