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Square Wave Voltammetry

Over the past several years, there has been a resurgence of interest in electroanalytical chemistry, and particularly in pulse voltammetry. A great deal of the impetus for this resurgence was the work, in the 1950s, of Geoffrey Barker in England and the development, in the late 1960s in the U.S., of the first practical high-sensitivity pulse voltammetric instrument, the PARC 174 (EG&G Princeton Applied Research). Whereas conventional dc polarographic techniques had detection limits of $\sim 10^{-5}$ M, the PARC 174, using differential pulse polarography, made it possible to attain detection limits that were easily two orders of magnitude lower. Until fairly recently, this and similar instruments, such as the IBM 225 voltammetric analyzer (IBM Instruments, Inc.), provided the best techniques in pulse voltammetry.

However, more recently—again stemming from the work of Barker in the 1950s—a new technique has arisen which, in our view, surpasses and thus will soon supplant differential pulse voltammetry as the ultimate voltammetric technique. This technique, square wave voltammetry, capitalizes on the present revolution in electronics, particularly the capability of per-

forming on-line computer-controlled experiments with both mini- and microcomputer systems. In this article we place square wave voltammetry in the context of voltammetry in general, describe the technique and its principle attributes, and give some examples that demonstrate its power as an analytical (or mechanistic) tool.

Voltammetry

Voltammetry (1-3) is concerned with the current-potential relationship in an electrochemical cell and, in particular, with the current-time response of an electrode at a controlled potential. If the potential is held—or stepped—to a value at which a faradaic process takes place involving the electrode and a solution species, then current flows and, with proper control of the experiment, the current can be used to determine the concentration of the solution species and to obtain information regarding the identifica-

tion of that species, though it must be stated at the outset that electrochemistry, by itself, is not a particularly useful tool for species identification. (The combination of electrochemistry coupled with chromatography, however, is a powerful tool for both qualitative and quantitative identification.)

The current is the rate at which charge passes through the electrode-solution interface. Current arising from a faradaic process is a direct measure of the rate of the process and, if the rate is proportional to concentration, it is also a measure of the concentration of solute species. The integrated current, or charge, is a measure of the total amount of material converted to another form. In some applications, e.g., stripping voltammetry and electrogravimetry, that charge may correspond to total removal of the solute species. However, in a typical voltammetric experiment, the amount of material actually removed,

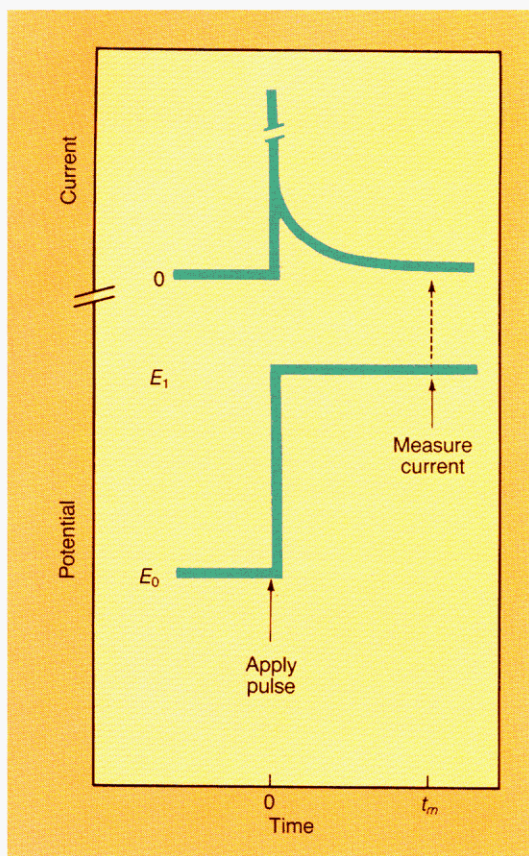


Figure 1. Potential pulse and current response showing sampling of the current at time t_m after pulse application. From Reference 16

or converted to another form, can be made quite small, so that even for very small sample volumes voltammetric techniques may be considered nondestructive.

Although the amount of material converted can be very small, large changes in concentration occur at the electrode surface during a redox reaction. In the general terms beloved by electroanalytical chemists



Further, these concentration changes depend on time; reactions at the electrode-solution interface create sharp concentration profiles that extend away from—or in the case of amalgam formers at a mercury electrode, into—the electrode. These sharp concentration profiles are smeared out with time, much as one can see the sharp boundary that occurs when one places a drop of red ink into water become more diffuse as the ink diffuses away from its injection point.

The time dependence of the concentration profiles near the electrode is manifested experimentally by currents that vary with time. This time dependence, a central feature of voltammetry, provides the possibility of great flexibility—the tailor-making of

techniques for specific problems—but also provides great scope for misunderstandings and missed opportunities. The central point is that every voltammetric experiment contains time as a parameter.

In some voltammetric techniques the time parameter is hidden, or at least obscured. In linear scan voltammetry, for instance, the current depends on scan rate, $\nu = dE/dt$, and in various kinds of hydrodynamic voltammetry (which features forced convection), the current depends on the solution flow rate. For the rotating-disk electrode, the time dependence is in the rotation rate of the disk, which in turn controls the solution velocity near the electrode. In pulse voltammetry, the time dependence appears explicitly as the width in time of the potential step that is applied to an electrode to cause the faradaic process to take place.

Techniques of pulse voltammetry are all based on what is called chronoamperometry, the measurement of current as a function of time after applying a potential pulse, as shown in Figure 1. Various types of waveforms actually used in pulse voltammetry are shown in Figure 2. *Effective application of routine techniques based on*

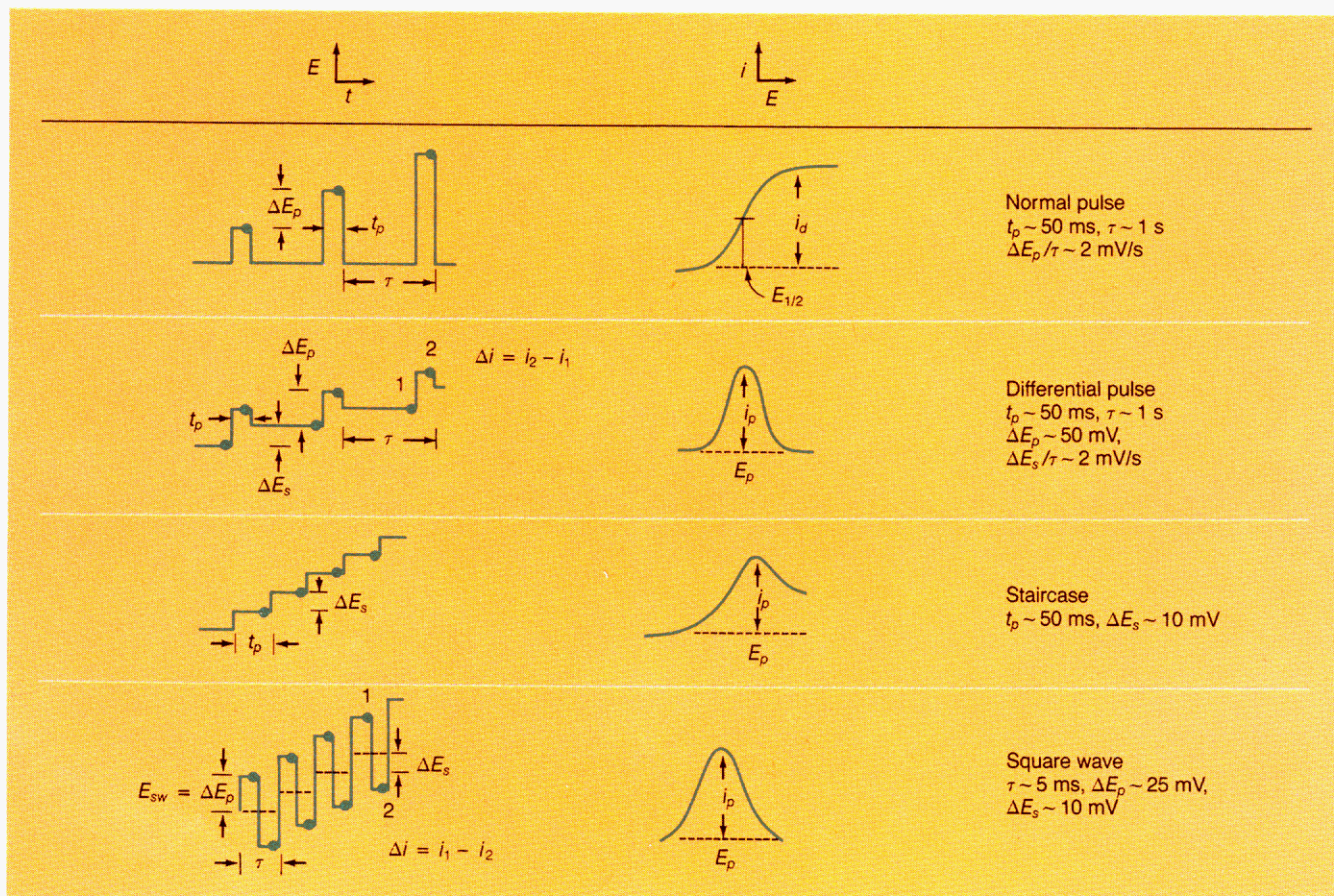


Figure 2. Description of pulse voltammetric techniques showing potential-time waveforms, current-sampling schemes, typical current-potential responses, and typical values of parameters

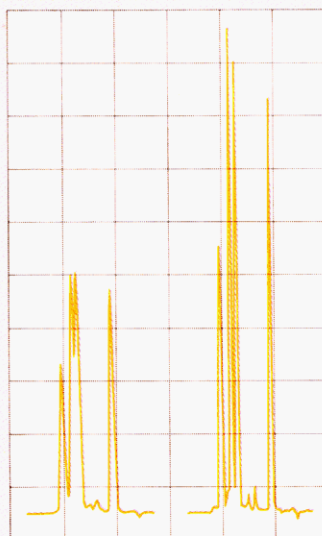
τ = waveform period (pulse repetition time); t_p = pulse width; ΔE_p = change in pulse potential; ΔE_s = step height; $E_{1/2}$ = half-wave potential; i_d = diffusion current; i_p = peak current; E_p = peak potential; and E_{sw} = square wave modulation potential. From Reference 16

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RIGHT: Rheodyne 7315 low-dispersion filter with 1 mm x 300 mm column.

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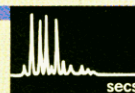
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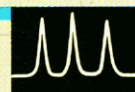
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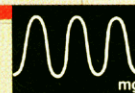
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chronoamperometry depends on inexpensive, reliable modern electronics for potential control, current measurement, and accurate timing in the millisecond time domain.

The electronic revolution is illustrated in this context by observing that in the early 1960s, a differential pulse polarograph developed by Barker and sold by Cambridge Instruments in England cost about \$25,000 in the U.S. When the PARC 174 was developed in about 1970, it originally sold for under \$2000. And this just illustrates the difference between vacuum tubes and transistors!

The ability to combine many chronoamperometric steps to attain a pulse voltammetric technique requires complex switching and logic circuitry to construct the potential-time waveform one desires to apply to the electrode and then to sample the resulting current response at some fixed, known time. Some feeling for the technical problems involved can be had by reading an entertaining account of the development of the PARC 170, the antecedent of the PARC 174, in Reference 4. These first-generation pulse voltammetric instruments performed a fixed set of experimental techniques quite well, but were inflexible because *hardware* fixed the sequence of events performed experimentally.

Although the use of computers to perform on-line experiments in electrochemistry is not especially new—we have ourselves been shaking that particular tree for about 20 years—the great breakthrough in instrumentation for pulse voltammetry is only now taking place with the development of relatively low cost *microprocessor*-controlled instruments (5). These provide the ability to generate an arbitrary time sequence of potential application and current sampling, a power heretofore available only to the specialist with a minicomputer system.

Normal pulse voltammetry, perhaps the simplest pulse voltammetric technique, is essentially sampled chronoamperometry; it employs a sequence of pulses separated in time under experimental conditions that ensure that the same boundary conditions—i.e., uniform concentration of material at the electrode surface and extending into the solution—prevail prior to each pulse application (see Figure 2). Therefore, the data can be analyzed by the simple, well-developed theories for single-step chronoamperometry. Complex combinations of potential steps produce a much more complex response that becomes inaccessible to theoretical treatment without the computational power of computers.

Early developments in numerical techniques of calculating the current

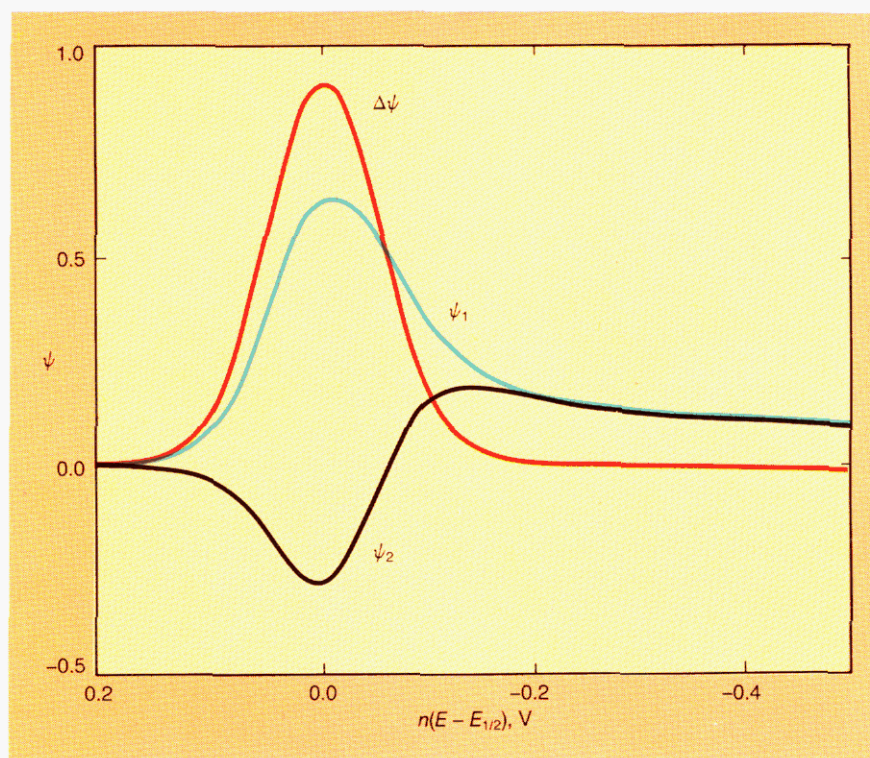


Figure 3. Normalized response for reversible process in square wave voltammetry. Normalized currents ψ_1 , ψ_2 , and $\Delta\psi$ correspond to currents i_1 , i_2 , and Δi shown in the square wave part of Figure 2. From Reference 9; vertical scale in the original figure is incorrect

response in linear scan voltammetry provide a classic example of how important such calculations are to the development and widespread use of a technique (6). These same numerical techniques make it possible to describe the theoretical current-time response to an arbitrary potential-time waveform and, therefore, provide the basis for analytical procedures and for studies of chemical and electrochemical processes.

Square wave voltammetry

In the early work by Barker, a small-amplitude square wave modulation imposed on a slowly varying dc potential was used at the dropping mercury electrode in what he, and the older literature, called square wave polarography. (Barker's awareness of the shortcomings of this technique led him to develop differential pulse polarography.) What we now term square wave voltammetry is a complex but powerful technique that required the power and flexibility of the minicomputer for its development and modern microprocessors for its commercial implementation. The square wave voltammetric waveform of Figure 2 combines a large-amplitude square wave modulation with a staircase waveform. The resulting net current (Δi , Figure 2), a true differential signal, can be obtained at high effective scan rates. The peak-shaped voltammograms obtained display excellent sensitivity and rejection of back-

ground currents. The main features of the voltammetric response are best illustrated by considering a simple, reversible redox system.

Square wave voltammetry for reversible electrode reactions. It is convenient to describe the current response in a pulse voltammetric technique in terms of a normalized current function. For a *simple, reversible* reaction, this current function depends *only on the potential sequence applied to the electrode, independent of time*. Also, provided a normalized potential scale is used, all reversible reactions have the same current function. The functional form of the familiar Nernst equation and the chronoamperometric response in normal pulse voltammetry suggest the definition

$$i = [nFAD^{1/2}C^b/\sqrt{\pi t_p}] \psi(\Delta E_s, E_{sw}) \quad (2)$$

In Equation 2, i is the measured current on each pulse; n is the number of electrons transferred; F is the Faraday constant; A is the area of the electrode; D is the reactant diffusion constant; C^b is the bulk concentration of the reactant; t_p is the pulse width (half the staircase period); the entire quantity in brackets is the maximum current that would be obtained with a normal pulse experiment under the same conditions; and ψ is the dimensionless current function, which depends on step height, ΔE_s , and square wave amplitude, E_{sw} (1-3). When this

normalized current function is plotted vs. the normalized potential, $n(E - E_{1/2})$, as in Figure 3, the resulting voltammogram is independent of pulse width, concentration, or identity of reactant, and so on. Thus one calculation of ψ can yield a whole family of voltammetric curves.

The quantity ψ or $\Delta\psi$ is simple in concept but unwieldy computationally, even for this simple case. Fortunately, the mathematical techniques for calculating ψ are well developed, and the expected responses for this and other more complicated cases have been published (7-9).

The current functions of Figure 3 can be identified with the experimental currents by referring to Figure 2. Curve ψ_1 (Figure 3) corresponds to the current measured at point 1 (Figure 2), curve ψ_2 to the current at 2, and $\Delta\psi$ corresponds to the net current, Δi . Currents ψ_1 and ψ_2 have qualitatively much the same diagnostic power as the forward and reverse currents in cyclic voltammetry.

The net current-voltage curve, Δi vs. E , or $\Delta\psi$ vs. $n(E - E_{1/2})$, is the most useful signal analytically. It is symmetrical about the half-wave potential, and the peak height is proportional to concentration. The shape of the net current voltammogram is remarkably insensitive to a variety of common complications of voltammetric experiments, such as complex electrode geometries or coupled homogeneous reactions.

The amplitude of the square wave modulation (E_{sw}) is so large— $50/n$ mV in Figure 3—that the reverse pulses cause reoxidation of the product (RED) produced on the forward pulses back to OX, with a resulting anodic current. Thus, the net current at its peak is larger than either the forward or reverse current, since it is the difference between them. Decreasing the magnitude of E_{sw} decreases the peak current without improving resolution significantly. On the other hand, increasing E_{sw} above $50/n$ mV broadens the peak without significant increase in peak height, i.e., sensitivity. Thus, independent of τ (the waveform period) or ΔE_s , the optimum sensitivity and resolution are obtained for $E_{sw} = 50/n$ mV for a reversible process. This relation holds for techniques such as differential pulse voltammetry as well.

The "real"—i.e., not normalized—current response depends on $t_p^{-1/2}$ or on $f^{1/2}$ (where $f = 1/\tau$), according to Equation 2. Thus, increasing the square wave frequency—equivalent to decreasing t_p —increases the square wave peak current and hence the sensitivity. Certain frequencies have more appeal than others; operation at 30 Hz tends to reject ubiquitous 60-Hz noise.

Operation at much higher frequencies (>1000 Hz) requires careful attention to cell design and electronics—particularly the current capability of the operational amplifiers. Roughly 200 Hz appears to be a reasonable trade-off between sensitivity and stable, trouble-free operation for more or less routine analytical work.

Advantages of speed. One of the advantages of square wave voltammetry is the ability to scan the voltage range of interest over one drop, if one is using a dropping mercury or static mercury drop electrode. The effective scan rate is $\Delta E_s/\tau$ or $f\Delta E_s$; thus, the time required to scan a potential range of ΔE_r is just $\tau(\Delta E_r/\Delta E_s)$. Very short experimental times can be achieved at moderate frequencies. For example, if $\Delta E_s = 10$ mV and $f = 200$ Hz, then the effective scan rate is 2 V s^{-1} , and the time required to scan 500 mV is only 0.25 s. The value of t_p is 2.5 ms which, in the chronoamperometric domain, is considered a reasonably fast pulse time. Thus, square wave voltammetry, at a 200-Hz square wave frequency and a ΔE_s of 10 mV, is a much faster technique, in terms of possible use in studies of electrochemical kinetics, than is suggested by its 2 V s^{-1} scan rate.

Suppose we consider the specific case of square wave *polarography*, i.e.,

voltammetry at the conventional dropping mercury electrode (DME) of classical polarography fame (or ill repute, depending on your viewpoint). Using a controlled drop time of 6 s, one could initiate the scan at the 5.5-s point and complete an entire potential scan of 1 V per drop using the parameters referred to in the preceding paragraph. In contrast, using differential pulse polarography, the same experiment would require 100 drops, or 600 s, with a marked decrease in sensitivity compared to square wave.

The direct comparison of square wave voltammetry with differential pulse polarography can tend to be misleading. Most commercial differential pulse voltammetric instruments sample the current approximately 50 ms after the application of the single pulse to each drop. To compare square wave in a similar time frame would mean using a 10-Hz square wave frequency, which is like requiring Wayne Gretzky (hockey fans, please take note) to skate backwards during an entire game.

Using a $50/n$ pulse amplitude for both techniques, and a 10-Hz square wave, the ratio of the peak current of the square wave voltammogram to that of the differential pulse would only be 1.3:1, or a 30% increase in sensitivity. However, at the very moder-

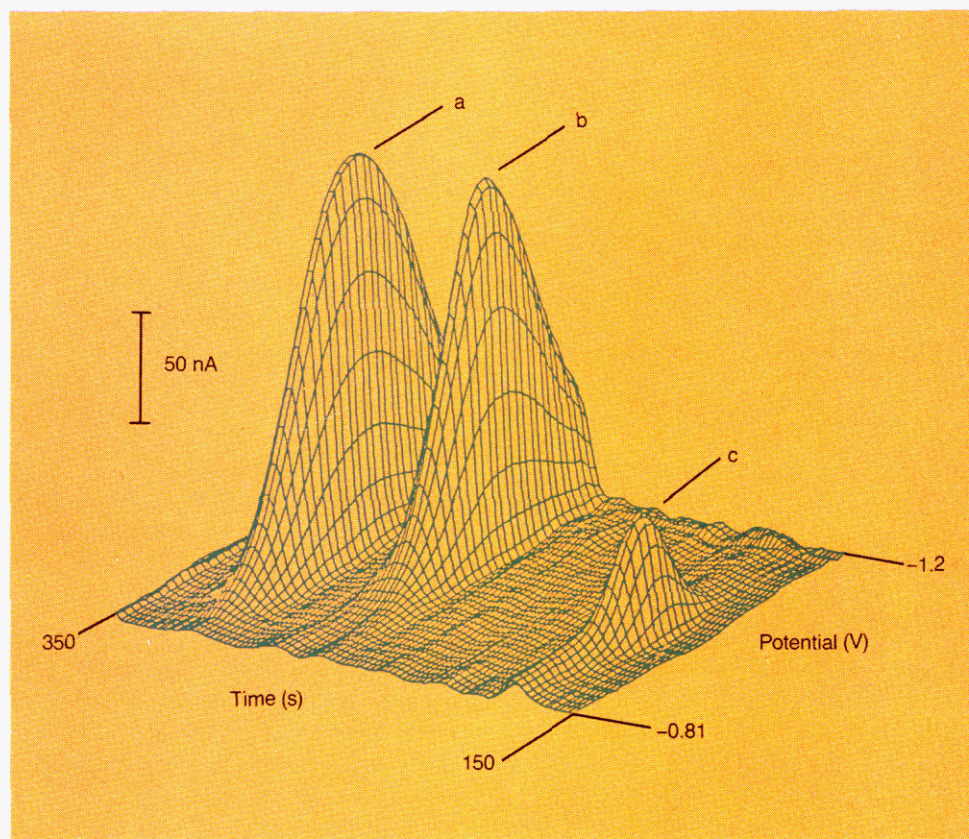


Figure 4. Three-dimensional square wave voltammograms of (a) *N*-nitrosoproline (13.4 μM) and (b) *N*-nitrosodiethanol amine (12 μM). The artifact (c) marks the time of injection

$E_s = 10$ mV, $E_{sw} = 25$ mV, $f = 100$ Hz, mobile phase 1% phosphate (pH 3.5). From Reference 13

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ate square wave frequency of 200 Hz, the ratio of peak currents would be 5.6:1, or a 560% increase in sensitivity. Coupled with that increase in sensitivity would also be about a 100:1 time advantage in doing the square wave experiment compared to the differential pulse experiment as described above.

The speed of square wave voltammetry and the practical necessity of operating under computer control for flexible choice of parameters make it possible to carry out identical experiments repetitively and average the results to increase signal-to-noise ratio. Averaging 25 replicates with a 2.4-s cycle (drop) time would require only 1 min but would in principle improve detection limits over those for one scan by a factor of five. High effective scan rates also decrease the quantity of charge passed, which in turn lessens the possibility of undesirable surface reactions.

An additional advantage of the fast-scan capability of square wave voltammetry is the ability to determine changes in the voltammetric response with time nondestructively. These may include changes due to homogeneous kinetics, as in synthetic reactions, to heterogeneous kinetics as in dissolution reactions, or to the mode of sample presentation, as in flow injection analysis and in electrochemical detectors for high-pressure liquid chromatography (HPLC). An example of the latter is shown in Figure 4. The quality of these voltammograms easily permits studies to be made on materials as they are eluted from the chromatographic column. In addition the voltammetric information adds further resolving power to the chromatographic separation.

Background currents. Not only does the differential current measurement scheme provide a convenient symmetrical peak, but perhaps more important the net current gives excellent rejection of background currents. In voltammetry, these background currents are typically large and thus often the critical factor in determining the detection limits.

The current measurement scheme of Figure 1 is designed to reject ac charging currents, and all of the techniques of Figure 2 normally do this well. The great virtue of square wave voltammetry is the rejection of any currents that are largely independent of potential. This feature is suggested by Figure 3 in which the net current in the limiting current region ($E \ll E_{1/2}$) is exactly zero. In trace analysis, oxygen reduction often produces unacceptably large and unstable background currents. But with square wave on the limiting current plateau for oxygen reduction these currents are automati-

Table I. Dimensionless peak current function for square wave ($\Delta\psi_{p,sw}$) and differential pulse ($\Delta\psi_{p,dp}$) voltammetry for various kinetic parameters^a

	$\Delta\psi_{p,sw}$	$\Delta\psi_{p,dp}$
$\kappa\tau^{1/2} = 100$ (reversible case)		
$\alpha = 0.3, 0.5, 0.7$	0.93	0.75
$\kappa\tau^{1/2} = 0.01$ (irreversible case)		
$\alpha = 0.3$	0.17	0.14
$\alpha = 0.5$	0.30	0.27
$\alpha = 0.7$	0.40	0.40

^a $nE_{sw} = 50$ mV, $\Delta E_s = 10$ mV, $\Delta E_{dp} = 100$ mV, $t_d/t_p = 100$ (differential pulse). The charge transfer coefficient α , the fraction of applied potential that accelerates the forward reaction, takes the values shown in the table.

cally subtracted.

The square wave net current is also insensitive to currents arising from convective mass transport as long as the characteristic time of that transport is large in comparison with the voltammetric pulse width. For example, in detection in HPLC, the net square wave signal is relatively insensitive to fluctuations in flow rate.

Square wave polarography presents a special case in that the primary source of background current is charging of the growing drop of the DME. Although this current is a function of potential as well as of time, the symmetrical current measurement scheme of square wave provides a good cancellation. Furthermore, this charging current depends on $t_d^{-1/3}$, where t_d is the drop time, or the charging current density depends on t_d^{-1} . Since an entire scan is carried out on one drop, one can use longer drop times to decrease the charging current.

A final type of capacitive current arises from the time variation of the capacitance itself. This may occur at a solid electrode as a result of a surface process or at mercury as the result of some adsorption process. If these processes are relatively slow, the square wave technique will still result in significant cancellation.

Effects of kinetics. Reversible charge transfer reactions are those for which the half-life for electron transfer is small in comparison with the characteristic time of the experiment (for square wave the pulse width, t_p). Under those conditions the concentrations at the electrode are determined thermodynamically, and the current is determined by potential and by the rate of mass transport to the electrode. On the other hand, when the characteristic time of the experiment is much less than the half-life for electron transfer, we say that the reaction is totally irreversible.

The relative importance of charge

transfer kinetics can be specified by the dimensionless parameter $\kappa\sqrt{\tau}$, where κ is an effective rate constant for charge transfer with units of $s^{-1/2}$, and τ is the square wave period. When $\kappa\sqrt{\tau} \gg 1$ the reaction behaves reversibly, while for $\kappa\sqrt{\tau} \ll 1$ it behaves totally irreversibly. As $\kappa\sqrt{\tau}$ decreases, for a square wave voltammogram (as for any other differential voltammogram), the differential peak current function ($\Delta\psi_p$) decreases to some minimum value, E_p moves to more negative values (for reductions), and the width of the peak increases to some maximum value. Since many reactions are irreversible, the lower values of $\Delta\psi_p$ in these cases represent a loss in sensitivity from the practical analytical point of view.

This point is worth some comment because of the incorrect notion, which persisted for some time, that square wave, like ac polarography as normally carried out, became very insensitive if used in the determination of solutes that react irreversibly. This is not the case, however; ac polarography usually employs small amplitudes—the modulating ac signal is ~2–10 mV. Large-amplitude ac would behave much the same way as square wave voltammetry in its response to irreversible solutes. Loss of sensitivity in square wave due to kinetic limitations depends on the exact choice of parameters, and it is therefore difficult to generalize. Some feeling for how minor this problem is can be obtained by comparison with the rather similar differential pulse case, as shown by the specific example of Table I. The reversible current for square wave is always greater than, and the irreversible current no less than, the corresponding differential pulse current. In either case the diminution in $\Delta\psi_p$ can be more than compensated for in i_p by decreasing the value of t_p if sensitivity is the limiting factor. Also note that since $\kappa\sqrt{\tau}$ depends on τ , a reaction can, in princi-

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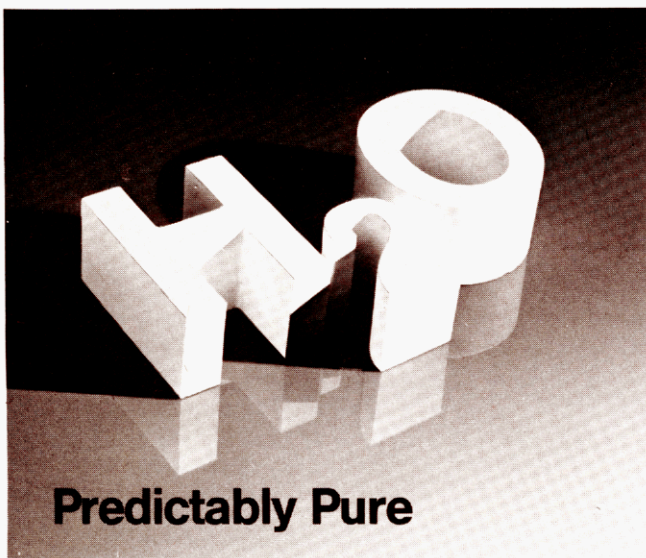
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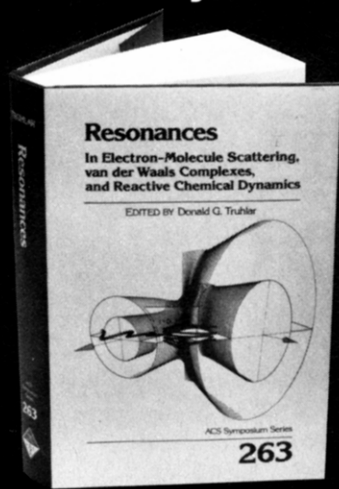
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ple, be moved through the kinetic range by appropriate choice of τ .

The theory for quasi-reversible square wave voltammograms has been published (9), and kinetic analysis has been carried out with *micromolar* solutes (10). This concentration is about three orders of magnitude lower than that normally used in such procedures. This is dramatic evidence of adequate sensitivity. However, the main attributes of the technique that permit accurate physical chemical studies at these levels of concentration are as described above: insensitivity to artifacts such as nonplanar diffusion, speed (which permits ensemble averaging), and good rejection of background currents. Comments made above referring to the use of square wave in electrochemical detectors for HPLC suggest that a detailed kinetic analysis of very small amounts of material, which may be unstable, is possible. For example, a 10- μ L detector volume in an HPLC electrochemical cell could be used to study the kinetics of a micromolar solution; that amounts to 10^{-11} mol of material. Some recent square wave applications can be found in References 11-19.

Square wave voltammetry, up to this point largely an academic pursuit in laboratories such as our own, will become more widely accessible as a result of the recent introduction of two commercial instruments capable of performing the technique, the Bioanalytical Systems BAS-100 and the Princeton Applied Research 384B. Both are microprocessor-based instruments, as required for the successful implementation of the technique. Both are multipurpose voltammetric instruments, though the PARC 384B is geared more to a routine analytical laboratory than the BAS-100. We suspect that a stand-alone square wave instrument will ultimately emerge.

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