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## Voltammetry for the Future

JANET OSTERYOUNG

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

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Pulse voltammetry comprises a suite of electrochemical techniques based on stepwise changes in the potential of an electrode together with sampling of current at known times in the potential sequence. The current is simply the rate of interfacial charge transfer and thus, properly normalized, the rate of the oxidation-reduction reaction that supplies or consumes electrons in the interfacial region. (This statement assumes that current due to Faradaic (i.e., charge transfer) processes can be separated in some way from capacitive (i.e., charge separation) processes.) Thus pulse voltammetry yields kinetic information. As for most rate measurements, an appropriate signal, properly referenced to standards, yields highly sensitive quantitative determinations as well. In this Account we describe these techniques and their application to problems in chemical kinetics and chemical analysis.

Pulse voltammetry has a long history going back to the early efforts of Kemula based on a mechanical switch.<sup>1</sup> More systematic development of mechanical devices for switching potential began soon after World War II, and finally the first electronic implementation of these ideas was achieved by Geoffrey Barker and co-workers, working at the Harwell Atomic Energy Research Establishment in the 1950s.

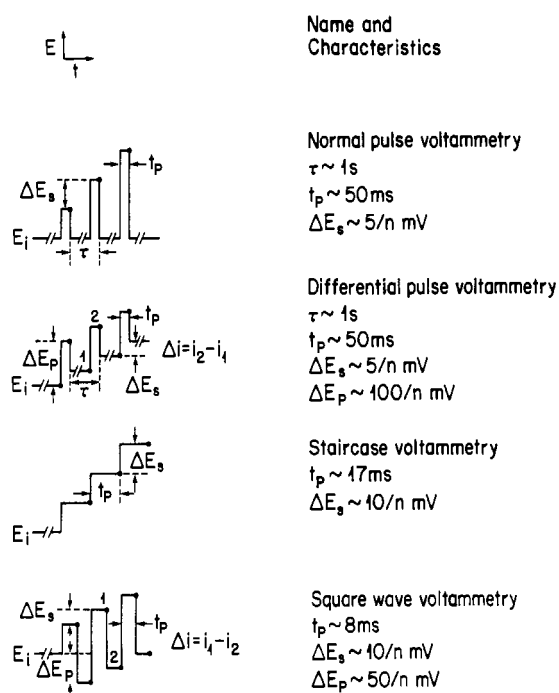
Barker's remarkable facility with instrumentation, combined with a theoretical bent and intuitive feel for

interfacial processes, laid the foundation for modern pulse voltammetric techniques. Unfortunately the main elaborations of his work are in AERE reports that are not generally available. Barker was also ahead of his time, in that the instruments he designed were based on vacuum tubes and thus by standards of even a decade later were expensive and unreliable. The subsequent commercial implementation of his ideas using solid-state electronic components essentially copied the function of the vacuum-tube-based instrument rather than basing new designs on the principles developed by Barker. These new instruments were marketed as chemical analyzers during the 1960s, when academic electrochemists turned decisively away from analysis and toward the study and control of interfacial processes. As a result of all of these factors, the capabilities of these techniques, both for chemical analysis and for kinetic measurements, were undervalued or not understood.

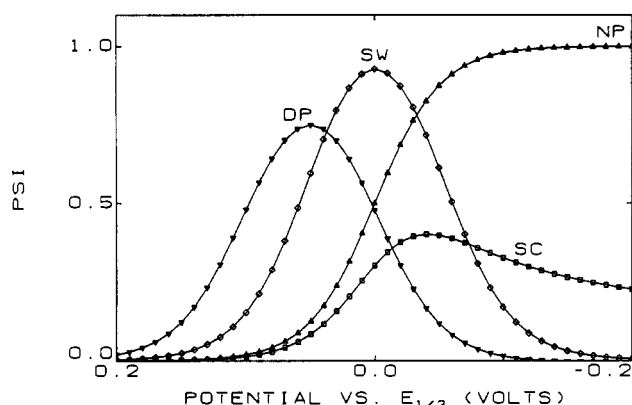
Today, 40 years after Barker's seminal work, we are in the midst of a revolution which is recreating almost daily new visions of what can be done using modern technology to elaborate on this general theme. The revolution that affects so dramatically the prospects of pulse voltammetry is driven by interconnected momentous changes in electronics, in computers, and in computation. To the extent that "modern voltammetry" comprises mainly the use and elaboration of "cyclic voltammetry", the purpose of this Account is to present a postmodernist view of pulse voltammetry and its applications.

Janet Osteryoung was born in Pittsburgh in 1939. She received the B.A. in chemistry with honors from Swarthmore College in 1961. She received the Ph.D. in chemistry in 1967 from the California Institute of Technology. She went to Montana State University as Assistant Professor of Chemistry in 1967 and to Colorado State University in 1968, where she held a variety of positions. She was Program Director for Chemical Analysis, NSF, in 1977-1978. She joined the Chemistry Department of SUNY/Buffalo as Associate Professor in 1979 and became Professor in 1982. She is presently Professor and Head, Department of Chemistry, at North Carolina State University. Her research interests include electroanalytical chemistry, analysis of complex materials, and the chemistry of natural waters. The main focus of the research is the investigation of chemical reactions requiring the development and elaboration of electroanalytical techniques, especially pulse voltammetry.

(1) Osteryoung, J.; Wechter, C. *Development of Pulse Polarography and Voltammetry*; Stock, J. T., Orna, M. E., Eds.; ACS Symposium Series 390; American Chemical Society: Washington, DC, 1989; pp 380-395.



**Figure 1.** Common pulse voltammetric wave forms and nominal values of voltammetric parameters. Heavy dots indicate the time at which current is sampled.  $\Delta E_s$  is the step height, the potential increment from one cycle to the next;  $\Delta E_p$  is the pulse amplitude, the amplitude of the modulation in a differential technique;  $t_p$  is the pulse width, the characteristic time;  $\tau$  is the period of one cycle.



**Figure 2.** Computed dimensionless response for the wave forms of Figure 1 for reversible charge transfer with semiinfinite planar diffusion: NP = normal pulse, DP = differential pulse, SC = staircase, SW = square wave (cf. Figure 1).  $\Delta E_s = 10$  mV,  $\Delta E_p = 100$  mV (DP), 50 mV (SW),  $n = 1$ . Note that the amplitude of the modulation is the same for DP and SW (cf. Figure 1).

## Pulse Voltammetry

Some widely used pulse voltammetric techniques are described in Figure 1, which shows for each the potential-time wave form with its parameters, together with some nominal values of the parameters employed in routine work. Optimization of a technique for a specific purpose consists in selecting the most favorable values of these parameters. Note that these are all constant potential techniques; that is, all changes in potential are discontinuities on the experimental time scale, and the current is sampled only after the potential has been constant for some time. Figure 2 displays the computed dimensionless response ( $\psi$  of eq 1 below) for these techniques for a simple reversible system. Of

these, the response for staircase is the most difficult to quantify, in that it displays neither a potential-independent region (as does the normal pulse response) nor a symmetrical (as in squarewave) or nearly symmetrical (as in differential pulse) peak characteristic of the differential techniques.

Note that staircase voltammetry can be viewed as the pulse or digital version of linear scan voltammetry. In linear scan voltammetry, potential is changed linearly with time, thus inextricably coupling the time and potential dependence of the response, as well as coupling the Faradaic response to the capacitive response occasioned by the change in potential with time. The linear scan or cyclic scan experiment is technically simple to implement and consequently has enjoyed widespread use and attention. The price paid for instrumental simplicity is 2-fold. First, the coupling of potential and time renders the theory of cyclic voltammetry complex. The model for even a simple reversible process has no closed-form solution and typically is elaborated as a numerical solution obtained by a finite difference estimation based on a discretized wave form. By way of contrast, the solution for a simple reversible process for staircase voltammetry can be written in closed form by inspection. Second, the application of linear scan voltammetry is restricted generally to a narrow range of concentration around 1 mM, the upper limit established by increasing distortion due to  $IR$  drop in solution, and the lower limit by increasing relative importance of capacitive current. In staircase voltammetry, time and potential are uncoupled by adding the parameter  $\Delta E_s$ , and all currents are measured at constant potential. Consequently there is no background current arising from change in potential with time, and measurements can be made at much lower concentrations. Returning to Figure 2, one might surmise from the shapes and amplitudes of the responses that, of the techniques referred to, staircase voltammetry is the least powerful. In fact, square-wave and normal pulse voltammetry are the most generally useful pulse techniques, and each routinely offers orders of magnitude improvements in the quality of data compared with that obtainable with linear scan or cyclic voltammetry.

The voltammetric techniques of Figure 1 and all others that employ only stepwise changes in potential are usefully grouped together under the one name of pulse voltammetry because the theoretical description of the response and the mode of application are the same. Consider first the theoretical description. It is convenient to describe the theoretical response by means of a dimensionless current function,  $\psi$ , which is related to the current,  $i$ , by a factor containing parameters of the experiment and the system under study:

$$i = nFAC^*(D/\pi t_p)^{1/2} \psi(nE(t); \bar{r}; \bar{k}) \quad (1)$$

where  $n$  is the number of electrons per unit reaction,  $F$  is the value of the Faraday constant,  $A$  is the electrode area,  $C^*$  is the bulk concentration and  $D$  is the diffusion coefficient of reactant,  $t_p$  is the pulse width (see Figure 1),  $E(t)$  describes the wave form,  $\bar{r}$  represents the geometry of the diffusion field, and  $\bar{k}$  represents thermodynamic and kinetic features of the model. The normalizing factor is the normal pulse diffusion-limited current (the current in the potential range where  $\psi =$

1, Figure 2),

$$i_d = nFAC^*(D/\pi t_p)^{1/2} \quad (2)$$

For all pulse voltammeteries and for many models, an implicit solution to the diffusion equation is

$$\psi(t) = \phi(t) - \lambda(t) \int_0^t \psi(u)(t-u)^{-1/2} du \quad (3)$$

The wave form enters into eq 3 only as numerical values of potential, which appear in  $\phi(t)$  and  $\lambda(t)$ . Therefore the functional form of the solution is independent of the choice of wave form.

Turn now to the practical aspect. Pulse voltammetry is best implemented by means of interactive control of the experiment through a computer or microprocessor. The principle of the implementation is that the user's choices of technique and values of parameters are translated into a table of numbers that specifies the values of potential, the periods for which they are applied, and the times current is sampled. Thus the way in which the experiment is carried out is independent of the choice of experiment.

This essential unity of mathematical formalism and experimental implementation puts the user in a strong position. The customary "modern" approach to voltammetric investigations is to employ one technique, cyclic voltammetry, and to interpret the results obtained. The postmodernist approach makes available a suite of pulse techniques, each in itself adaptable and each especially well suited to the investigation of a particular type of problem. Thus, instead of tying oneself to cyclic voltammetry, one can focus on the chemical problem, pose a question, and select a particular pulse technique with particular choices of parameters, the response to which emphasizes those features important to the question and discriminates against extraneous factors.

Were this a comprehensive review, this would be the logical point at which to begin a systematic comparative discussion of the attributes and merits of the various pulse techniques. As it is not, we elect rather to instruct (and perhaps allure) the reader by means of examples. First, however, we return to the technical basis for the present and projected power of these techniques.

### The Revolution

The triple support of electronics, computers, and computation forms a kinematic mount for pulse voltammetry. The absence of one reduces the power of at least some pulse techniques in some applications to merely competitive performance. Every reader is familiar with momentous improvements in electronic performance, computing power, and the development of algorithms. Not so obvious is the way in which quantitative improvements may combine to place in the hands of an average user, in a practical way, the power and flexibility of the suite of pulse voltammetric techniques.

Modern graphics capabilities provide instant display of the experimental result. This is essential for troubleshooting, but it is even more important for providing instant gratification and reinforcement of the itch to experiment. Read-only memories and dedicated microprocessors can handle the involved timing and synchronization required over the range of

pulse voltammetry in a way which is largely transparent. This is remarkable considering that the dynamic range of the time scale can be as large as  $10^7$ . Enormous increases in computing power per unit cost make it feasible to carry out involved calculations in "real time" on the same simple laboratory computer which controls the experiment. Interlocking developments in new algorithms and computing power create a practical means of analyzing complex data, again by means transparent to the user.

The latter point requires some elaboration. In all linear scan voltammetric experiments the potential is changed linearly with time from an initial value to a final value. Changes in the rate of scan do not create a different experiment. Any instrument which carries out faithfully this simple perturbation yields in principle a result which can be analyzed according to a model which employs that perturbation. This is an important reason for the success and resulting popularity of the modeling approaches used to interpret the results of linear scan voltammetry. These approaches have also been developed for and applied to single potential step chronoamperometry, in which, again, the physical experiment and the assumptions of the model can be made to coincide over reasonable ranges of time scale.

Pulse voltammetry is by comparison dauntingly complex. Within this framework one has thousands of different practical possibilities, and the fidelity with which any instrument produces an idealized wave form and samples synchronously the instantaneous current depends on the experiment and the time scale. For example, suppose that for technical reasons current is sampled over an aperture of 1 ms at the end of each pulse. This current can be treated for theoretical purposes as an instantaneous current measured at the end of the pulse, if the pulse width is much greater than 1 ms. For shorter pulse widths one must consider both the finite width and the change in the location of the aperture.

Many technical factors such as this, together with the wide choice of wave forms and their parameters, create a qualitatively new situation not well handled by the conventional "modern" ways of treating voltammetric data. Fortunately, affordable computing power provides a means by which one can, using the computer which controls the experiment, induce the voltammogram to yield its secrets in "real time". Furthermore, by binding together in one system the implementation of the experiment and analysis of the result, one avoids the trivial but disastrous mistake of comparing the model for one wave form with the response to a slightly different wave form.

### Analysis of Data

The dimensionless current function,  $\psi(nE(t); \bar{r}; \bar{k})$ , of eq 1 can be calculated or estimated by simulation for many geometries and kinetic models. The computation of  $\psi$  is itself not new; the practice of modern voltammetry relies on extensive modeling efforts. For the routine user, this theoretical basis is most often expressed through so-called working curves, that is, curves which express the dependence of  $\psi$  on a dimensionless kinetic parameter. For linear scan voltammetry this presents a simple and practical way to estimate rate constants. For pulse voltammetry, in

contrast, because of the flexibility of the experiment, the approach of working curves is impractical, for a special set of curves would be needed for every change in the (normalized) wave form.

Efficient algorithms and computing power have created the possibility of basing the analysis of data on contemporaneous computation of  $\psi$ . This is accomplished by means of a statistically well founded method of nonlinear least squares formally equivalent to the method of maximum likelihood.<sup>2</sup> The experimental current is assumed to be a linear function of the dimensionless theoretical current with a normal distribution of errors:

$$i(t) = a\psi(nE(t); \bar{r}; \bar{k}) + b + \epsilon(0; \sigma) \quad (4)$$

The quantity  $b$  allows for an offset in the experimental current. Comparing with eqs 1 and 2, if the model is correct the slope  $a$  is equal to the normalizing factor,  $a = i_d$ , which renders the theoretical current dimensionless. This formulation of eq 4 separates the linear from the nonlinear parts of the problem, which makes the computation efficient. Following an initial guess of the values of the unknown parameters that determine  $\psi$ , and initial step sizes, an opportunistic search is carried out to locate the values of parameters that result in the maximum value of the correlation coefficient of the linear relation of eq 4. These optimal values of the parameters are those which give statistically the best fit of the theory to the experiment.

This method employs all of the data from a single voltammogram. It does not require that one know the exact zero of current (an irritatingly difficult requirement) or that one use other information to normalize the data. The functions  $\psi$  display strong unimodality and thus yield false minima only when the noise is comparable in magnitude to the effect which is sought. This method also provides the means for computing statistically rigorous regions of confidence for the values of the parameters. This approach to the analysis of electrochemical data has been described in detail and is referred to as the COOL algorithm.<sup>2</sup>

### Electrochemical Kinetics

Recall that the voltammetric current is a measure of the rate of heterogeneous charge transfer. For a simple process in which the charge-transfer step is rate determining, the kinetic phenomenon (i.e., the voltammogram) is described by a function of the three parameters,  $\log \kappa t_p^{1/2}$ ,  $\alpha$ , and  $E_{1/2}^r$ . The quantity  $\kappa$  ( $s^{-1/2}$ ) is proportional to the standard rate constant; the quantity  $\alpha$  expresses the potential dependence of the rate; and  $E_{1/2}^r$ , the reversible half-wave potential, is a measure of the standard potential for the reaction. Good instruments provide the possibility of measuring the standard rate constant with relative precision of 0.2% and the standard potential with absolute precision of 0.1 mV. We routinely achieve this precision through analysis of single voltammograms by means of the COOL algorithm.

In practical voltammetric measurements one is usually happy with a precision of 50% in rate constant and

2–3 mV in potential. The difficulty in replicating the electrochemical system is usually the main factor which causes the rate constant to be much less precise than the current measurement. Difficulties in maintaining an adequate laboratory reference potential generally dominate the uncertainty in potential. For example, saturated calomel electrodes display temperature coefficients of ca. 0.25 mV K<sup>-1</sup> and large hysteresis. Unless an electrode is maintained at fixed temperature continuously, the combination of diurnal variation of ambient temperature, slow attainment of thermal equilibrium, and hysteresis can produce variations of 2–3 mV in the reference potential over time. Methods of data analysis which require an independent determination of  $E_{1/2}^r$  necessarily mix together data from different experiments, which distorts the potential scale. There is great advantage therefore in determining rate parameters from the data contained in one short experiment. In that case, although the chemical system may be less well specified than one would prefer, at least it is one chemical system. Drift of the system during the experiment can be eliminated by making the experiment short. Thus difficulties with the reference potential result only in translation, not distortion, of the potential scale. This is crucial if the main information sought is the potential dependence of the rate.

Methods which require normalization of the current scale have the same effect. Here the information required, at least conceptually, is the diffusion-limited current,  $i_d$  (eq 2). Slight errors in the zero of current create large errors in the normalized current for small values of  $i/i_d$ , and small errors in  $i_d$  create disastrous errors in  $i/i_d$  for values near unity. These errors are inherent in the approach itself and cannot be eliminated by careful attention to detail.

The combination of pulse voltammetry with the COOL algorithm provides a means for acquiring kinetic information free of these artifacts. Square-wave voltammetry has special virtues as a technique for investigations of charge-transfer reactions.<sup>4</sup> In square-wave voltammetry, all pulses are of nearly equal amplitude (the forward-going pulse having amplitude  $2\Delta E_p + \Delta E_s$ , the reverse pulse  $2\Delta E_p$ , cf. Figure 1). As a result, when the net current ( $i_1 - i_2$  cf. Figure 1) is employed, currents not due to the process of interest tend to cancel. In particular, the shape of the net current response is largely independent of the effects of nonplanar diffusion and convection.<sup>5</sup> The net current thus provides a faithful record of the rate of the process which is being studied.

Figure 3 presents values of the kinetic parameters for reduction of Zn(II) in 1.0 M KNO<sub>3</sub> obtained from normal pulse voltammetry.<sup>6</sup> The range of concentration of Zn(II) is 1 mM–1  $\mu$ M. At each concentration the values of  $-\log \kappa t_p^{1/2}$ ,  $\alpha$ , and  $E_{1/2}^r$  are obtained by analysis of individual voltammograms according to the COOL algorithm. The values and ranges at 1 mM Zn(II) are averages and standard deviations of five replicates. For the lower concentrations, the values are inferred from individual voltammograms by means of the COOL

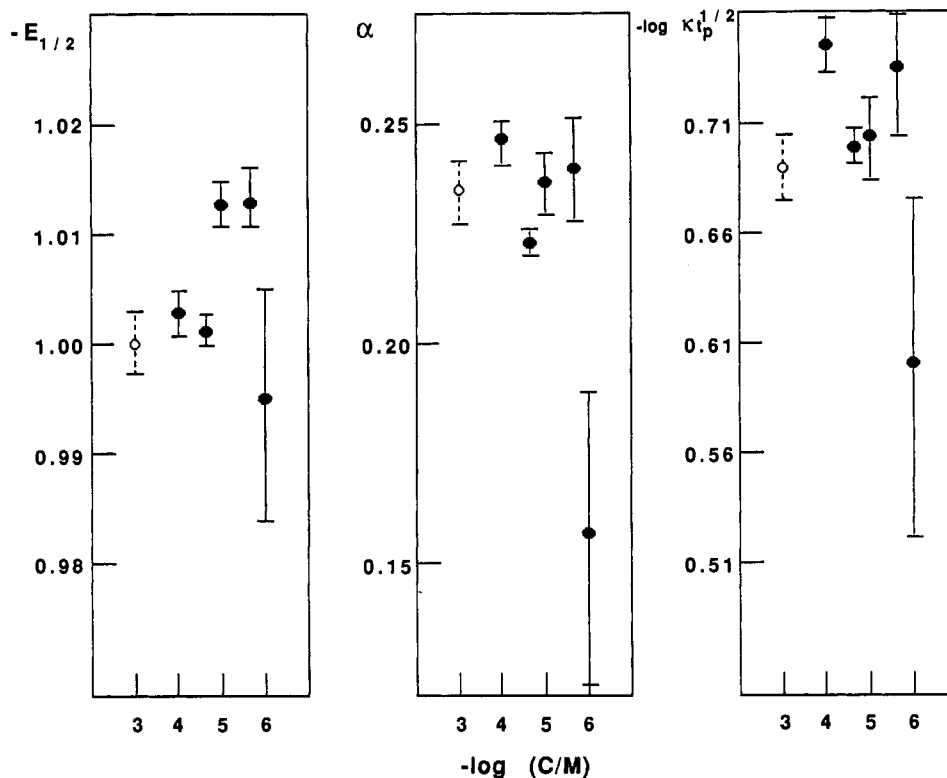
(2) O'Dea, J. J.; Osteryoung, J. G.; Lane, T. *J. Phys. Chem.* **1986**, *90*, 2761–2764.

(3) Osteryoung, J. G. *Chemometrics Intell. Lab. Sys.*, **1991**, *10*, 141–154.

(4) Go, W.; O'Dea, J. J.; Osteryoung, J. G. *J. Electroanal. Chem.* **1988**, *255*, 21–44.

(5) Aoki, K.; Tokuda, K.; Matsuda, H.; Osteryoung, J. *J. Electroanal. Chem.* **1986**, *207*, 25–39.

(6) Go, W. Ph.D. Dissertation, SUNY Buffalo, 1987.



**Figure 3.** Kinetic parameters for reduction of Zn(II) at Hg derived from normal pulse voltammograms by the COOL algorithm at various concentrations of Zn(II).  $E_{1/2}^r$  is the reversible half-wave potential;  $\alpha$  is the charge-transfer coefficient; and  $\kappa$  is a normalized standard rate constant,  $\kappa = k^0 D_O^{-(1-\alpha)/2} D_R^{-\alpha/2}$ ; Zn(NO<sub>3</sub>)<sub>2</sub> in 1.0 M KNO<sub>3</sub>; static mercury drop electrode; delay time 5 s; pulse width 20 ms; step height 5 mV; range  $-0.850$  to  $-1.350$  V vs SCE; (O) average optimal value from five voltammograms (dashed vertical line indicates standard deviation); (●) optimal value from individual voltammogram computed by means of the COOL algorithm (solid vertical lines indicate extent of confidence region at the optimal value and orthogonal to the other coordinates).

algorithm, and the error bars are the dimensions of the 95% confidence ellipsoid of the point ( $\hat{E}_{1/2}^r, \hat{\alpha}, \log \hat{\kappa} t_p^{1/2}$ ). (For example, for  $\hat{E}_{1/2}^r$ , the error bars are defined by the points on the  $\hat{E}_{1/2}^r$ -axis which intersect the confidence ellipsoid.)

Tamamushi reports 69 transient studies of the kinetics of reduction of Zn(II) in aqueous solution.<sup>7</sup> The concentration ranges from 0.25 to 5 mM, and in no one study is the concentration varied. The main reason the concentration is fixed is that each particular experimental situation demanded for adequate functioning a very narrow range of concentration. In Figure 3 the nominal condition is a concentration of 1 mM, and the uncertainties, expressed as standard deviations of replicates, are rather low for work of this type. Note that the absolute error of the logarithm of the dimensionless standard rate constant gives the relative error in the standard rate constant, which, for 1 mM, here is about 3%. In the middle range of concentration, 0.1–0.01 mM, the uncertainty is somewhat less. That is, the theory matches experiment more closely than the experiment can be replicated. At 5  $\mu$ M concentration the quality of the result is indistinguishable from that at 1 mM. Note that the data for 5 and 10  $\mu$ M display apparently anomalous values of  $E_{1/2}^r$ ; however, because  $E_{1/2}^r$  is treated as an unknown and data from only one voltammogram are used, this does not propagate into incorrect values of  $\alpha$  or  $\log \kappa t_p^{1/2}$ . At 1  $\mu$ M, one is approaching the empirical detection limit for Zn(II) under these conditions. The uncertainty in  $E_{1/2}^r$

becomes unacceptably large, while the uncertainty in the rate constant increases to about 20%. The real shocker is  $\alpha$ : because the response depends exponentially on  $\alpha$ ,  $\alpha$  is the first to display the degradation of kinetic information in the response as the noise in the net signal (that in the presence of Zn(II) less than in its absence) approaches the magnitude of the kinetic effect.

Refer back to eq 4. From the analytical point of view, this expresses the calibration curve, that is, the signal is  $i$  and the quantity sought is  $a$  ( $=i_d$ , proportional to  $C^*$ ). Approaching the detection limit,  $a$  becomes smaller, and both  $b$  and  $\epsilon$  confound attempts to use  $i$  as a measure of  $a$ . The kinetic problem is the same; that is, one wishes to use  $i$  as a measure of  $\psi$ , and for sufficiently small values of  $a$ , the term  $a\psi$ , and thus  $\psi$ , becomes indeterminate. The initial popularity of pulse voltammetry lay in the ability of these techniques to reduce  $b$  and provide large values of  $\psi$  (or  $\psi t_p^{-1/2}$ , cf. eq 1), and thus to yield low detection limits. By the argument given above, any voltammetric technique should provide, with proper analysis of the signal, kinetic characterization at concentration levels near the detection limit. The reason that pulse voltammetric techniques can provide kinetic characterization at micromolar levels of concentration is that they generally provide excellent detection limits.

In the foregoing we have illustrated the power of pulse voltammetry as a tool for investigating electrochemical kinetic processes and have emphasized the rejection of features of the response not included in the kinetic model and the ability to vary over a wide range the

(7) Tamamushi, R. *Kinetic Parameters of Electrode Reactions of Metallic Compounds*; IUPAC, Butterworths: London, 1975.

parameters of the system. The model has not been discussed at all.

Let us turn to a second kinetic example, which illustrates the power of these techniques to test the suitability of the model. It should be emphasized that it is our intention to deal only with phenomenology, that is, we wish to know if the model explains all of the variation in the data. We do not address the more ethereal issue of describing a mechanism which gives rise uniquely to the model.

We have examined recently the reduction of adsorbed species with an interest in developing both an understanding of the reduction process and a method for quantitative determination of the amount. The compounds of interest are benzodiazepines, in particular the psychotropic drugs of this class. For a representative, midazolam, square-wave voltammograms fit the model for first-order, totally irreversible reduction. Over the range from 1 to 20 mV in step height (refer to Figure 1), from 0 to 100 mV in square-wave amplitude, 10 to 1000 Hz in frequency, and 1 to 90 s in time for adsorbate to accumulate, the signal changes by 100-fold but deviates from the model in each case by no more than 0.5%. However, the resulting values of  $\alpha$  and of dimensionless rate constant display strong trends with change in frequency. For example, the value of  $\alpha$  changes from 0.66 to 0.75 as the frequency changes from 1000 to 10 Hz, whereas the uncertainty in the derived values, as estimated from the confidence ellipsoids, is no more than 0.01. As a result we can conclude that the model is incomplete, even though the model fits the data for each experiment within the precision of measurement. In this case pulse voltammetry provides the capability to achieve precise and accurate measurements over wide ranges of conditions, and the COOL algorithm provides a rigorous estimation of the uncertainty of the derived parameters. The combination allows us to reach a powerful conclusion based on detailed quantitative investigation.

### Electrochemical Analysis

Theories of chemical analysis deal with concepts such as calibration, noise, sensitivity, and so on. The analytical approach to determination of concentration by instrumental methods deals with the relation

$$S = kC + d \quad (5)$$

where  $S$  is the signal,  $k$  the sensitivity, and  $d$  the "background". Theory aids the process of improving and assessing the quality of analytical results mainly by dealing with the applied statistics of this relation.

For most instrumental techniques the sensitivity cannot be predicted reliably from the properties of the analyte and the parameters of the experiment. For example, in the case of UV absorption spectrophotometry,  $k = \epsilon l$ , where  $\epsilon$  is the molar absorptivity and  $l$  the path length. In principle, the molecular structure of the absorbing species is known, and the molar absorptivity can be calculated, but in practice,  $k$  is always found by measuring the absorbance of solutions of known composition.

By comparing eq 5 with eqs 4 and 1 we see that in the case of pulse voltammetry we may replace the notion of calibration curve with the theoretical formulation of eq 4. Thus, if the reaction mechanism is known,  $a$  can

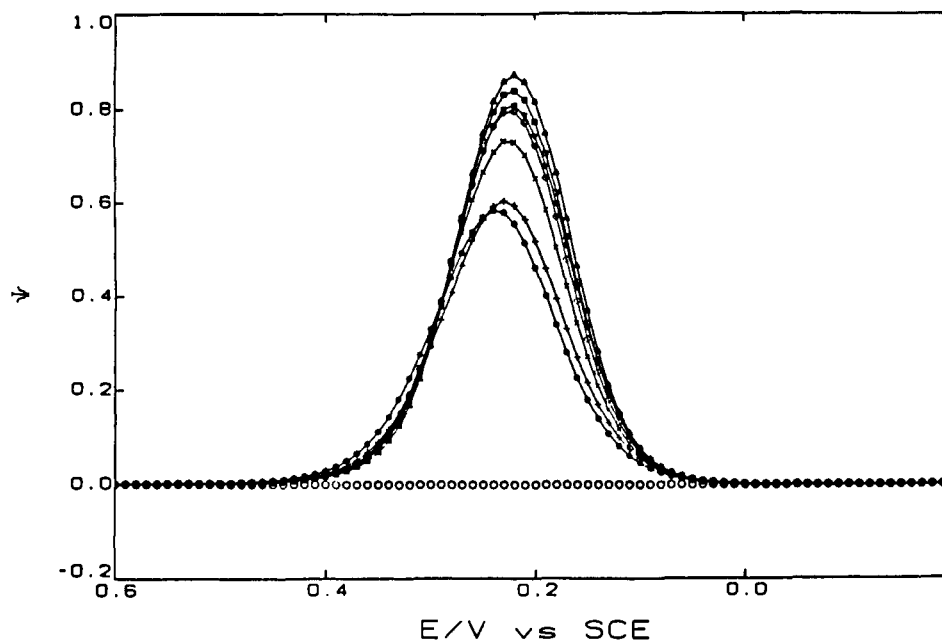
be obtained from a voltammogram by means of the COOL algorithm by using the theories of pulse voltammetry.

The calibrating factor  $nFA(D/\pi t_p)^{1/2} = a/C^*$  contains parameters of the experiment (electrode area,  $A$ ; pulse duration,  $t_p$ ) which are known and those of the system (the number of electrons per unit of reaction,  $n$ ; the diffusion coefficient of reactant,  $D$ ) which may be known and can be estimated. This factor does not depend strongly on other conditions of the experiment. Thus the relation between  $a$  and  $C^*$  may be obtained by calibration or may be estimated by direct calculation.

The approach to analytical information through eq 4 rather than eq 5 opens the possibility of resolving the dilemma of voltammetric measurements presented by the large magnitude of background currents. Pulse voltammetry as a suite of techniques attempts to diminish capacitive current compared with Faradaic current by measuring all currents at constant potential (thus avoiding capacitive current from  $dE/dt$  so prominent in cyclic voltammetry) and by measuring current at a time after each pulse that is large compared with the  $RC$  time constant of the system. This strategy diminishes capacitive current but does not reduce other background currents. For example, the current due to reduction of oxygen, which occurs at negative potential, cannot be reduced much below  $1 \mu\text{A s}^{1/2} \text{ cm}^{-2}$  in deoxygenated solutions (outside of a glovebox). As another example, solid electrodes often display currents due to surface processes that are inherent. These background currents can be diminished with little loss of sensitivity by modulating the potential, as for example in square-wave voltammetry (Figure 1), and using the difference current as the response.

The difference current of square-wave voltammetry behaves like a derivative and thus has its maximal value at the potential where current and, thus, reaction rate change most rapidly with potential. In this region the difference current is most sensitive to other kinetic limitations such as slow charge transfer or slow homogeneous processes coupled with charge transfer. Thus differential techniques reject background current but are subject to wide variation in the calibrating factor,  $k$ , arising from kinetic factors. The objective of voltammetric methods development is often to find conditions for which the rate-determining process is transport of the reactant to the electrode. Then  $\psi$  is a simple function of the parameters of the experiment, and thus  $k$  is more likely to be constant reliably from sample to sample.

The two main sources of sample-to-sample variability in  $k$  are variation in composition of the sample and temporal changes in the electrode surface. Aqueous samples often contain small amounts of surface-active substances that are concentrated at the surface of the electrode and affect the kinetics of the charge-transfer process. This problem can be approached analytically by a prior cleanup step, but each such elaboration of an analytical procedure is costly in both time and money and, furthermore, may alter or contaminate the sample. Electrode materials themselves undergo chemical or electrochemical reactions, thereby changing properties with respect to charge-transfer kinetics from sample to sample. The success of the mercury electrode, despite the inconvenience or perceived danger of working with



**Figure 4.** Dimensionless optimal square-wave voltammograms for oxidation of 5 mM ferrocyanide in 1 M  $\text{KNO}_3$  obtained from the data by the COOL algorithm: glassy carbon electrode,  $A = 0.080 \text{ cm}^2$ ; step height 10 mV; square-wave amplitude 25 mV. Frequency/Hz: ( $\blacktriangle$ ) 5, ( $\square$ ) 15, ( $\blacktriangledown$ ) 25, ( $\diamond$ ) 50, ( $\times$ ) 100, ( $+$ ) 200, ( $*$ ) 500.

liquid mercury, is due to the ease with which the surface can be renewed automatically and reproducibly before each experiment. Much of analytical methods development with solid electrodes centers on gaining control of the electrode surface. Notable success notwithstanding,<sup>8,9</sup> this has been a dispiriting field of endeavor.

The formulation of eq 4 combined with the facile optimization afforded by the COOL algorithm resolves the dilemma posed by the dual requirement of rejection of background and insensitivity to kinetic factors. The variation in  $k$  due to kinetic factors is expressed by variation in  $\psi$ . A simple model of slow charge transfer fits a wide range of complex mechanisms.<sup>10</sup> The analytical response is fit by the COOL algorithm for the appropriate technique and this model to yield  $\psi$  and  $\alpha$  directly. The diffusion coefficient (cf. eq 1) is viewed as an unknown. Calibration consists in determining  $\alpha$ , thus  $D$ , by voltammetry of solutions of known composition.

Figure 4 displays a result which illustrates the power of this approach.<sup>11</sup> Optimal dimensionless voltammograms are displayed for oxidation of ferrocyanide at various frequencies. These are the theoretical voltammograms which are the best fits to the experimental voltammograms. Recall that the voltammogram depends on a dimensionless kinetic parameter,  $\kappa t_p^{1/2}$ . Variation in composition of samples generally causes variation in  $\kappa$ . In this experiment we employ the same sample but vary  $t_p$  in order to examine the change in the dimensionless response with change in the dimensionless kinetic parameter. The maximal value of  $\psi$  in Figure 4 varies by about 40% with 10-fold change in  $\kappa t_p^{1/2}$ . This same variation is seen in the maximal current, which would be expressed in terms of eq 5 as a 40% variation in  $k$ . However the quantity  $\alpha t_p^{1/2}$ ,

obtained from eq 4, which is predicted to be constant, varies by only 2%. Thus the COOL algorithm provides an analysis of the data which yields, even in this complex situation, accurate and precise values of concentration.

The idea of extracting from voltammetric measurements both kinetic and analytical information in "real time" is not new. Smith and his co-workers proposed and implemented a different approach to this objective 15 years ago.<sup>12</sup> That approach did not influence analytical practice, because it was not marketable as a cost-effective tool for routine analysis. The ensuing years of development have created a technical environment wherein square-wave voltammetry coupled with the COOL algorithm can provide a financially attractive analytical strategy based on relaxing the requirements of method development and decreasing the fraction of analyses required for calibration.

### Concluding Remarks

Examples have been presented here of the application of pulse voltammetry, combined with a comprehensive approach to analysis of the resulting data, to chemical problems. The treatment of data is classically statistical, in that one is condensing the data (e.g., from 200 pairs of numbers,  $(i, E)$ , to one quartet of numbers,  $\kappa, \alpha, E_{1/2}; a$ ) in real time. The advantages of this approach are experimental flexibility, statistical rigor, and instant gratification. In the past the technical complexity of these techniques has overshadowed their power and thus inhibited their use. Now improvements in electronics, computers, and algorithms have combined to render these complexities transparent and thus make the suite of pulse voltammetric techniques available to the user in a practical way.

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