

## CYCLIC DIFFERENTIAL PULSE VOLTAMMETRY: A VERSATILE INSTRUMENTAL APPROACH USING A COMPUTERIZED SYSTEM

KENNETH F. DRAKE and RICHARD P. VAN DUYNÉ \*

*Department of Chemistry, Northwestern University, Evanston, Ill. 60201 (U.S.A.)*

ALAN M. BOND

*Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052 (Australia)*

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### ABSTRACT

An extremely versatile instrumental approach in differential pulse voltammetry using computerized instrumentation is described. Scan rates in excess of  $1 \text{ V s}^{-1}$  can be used and each of the d.c. (staircase), pulse, and differential pulse components of the experiment can be measured simultaneously. Measurement of the individual components of this dual time domain technique rather than just the differential readout is shown to provide important additional information concerning both the nature of the technique and the electrode process under consideration. The use of cyclic differential pulse voltammetry is also described and shown to be a valuable extension to the currently available methodology in differential pulse voltammetry. An upper useful limit in the scan rate of about  $1 \text{ V s}^{-1}$  is imposed on the technique because of the d.c. faradaic distortion terms arising from the d.c. (staircase) component of the experiment and for other reasons.

### INTRODUCTION

The technique of d.c. cyclic voltammetry is one of the most widely used electroanalytical methods for qualitative studies of electrode processes [1–3]. Techniques of d.c. voltammetry have also been employed extensively in quantitative analysis [4], especially using just one scan direction of potential, where the technique is now usually referred to as linear sweep voltammetry. The driving force for its use in analytical work is the time saved by the fast potential sweep compared with polarography at a dropping mercury electrode, and, of course, the fact that unlike polarography it can be used at solid electrodes. In electrode kinetic studies, quantitative use of cyclic or linear sweep methods is restricted by the need to interpret the inconveniently shaped asymmetric  $i-E$  curves in the presence of considerable charging current, particularly at the faster scan rates. To minimize the charging current difficulties, a staircase potential ramp can be used instead of a linear one and the technique of staircase voltammetry has received some attention in the literature [5–10]. Further-

\* Alfred P. Sloan Fellow 1974–1978.

more, the staircase waveform is ideally suited to digital rather than analog generation and to computer control so that much of this work has been coupled with the development of digital potential generators and computerized instrumentation. However, despite the different waveform, the shape of staircase voltammograms is similar to that of linear sweep curves, and this feature still detracts from the use of the technique.

Differential pulse polarography, in which a pulse is periodically imposed on the d.c. ramp and the difference in current before and after its application is plotted as a function of d.c. potential, has rapidly gained widespread appeal in analytical work [11]. This technique provides substantial discrimination against charging current and provides an ideal, peak-shaped curve which is very suitable for automated readout with computerized instrumentation as witnessed by the development of a commercially available microprocessor controlled instrument [12]. Osteryoung et al. [13,14] have performed a detailed evaluation of various options in differential pulse polarography, predominantly in the context of analytical applications using computerized instrumentation [14]. However, until recently [15], very little theoretical work, apart from examination of the reversible case, has been performed, and the use of differential pulse polarography as a technique for studying electrode processes has been extremely rare.

At stationary electrodes, the major stimulus for applying the differential pulse waveform has been for using the technique in conjunction with anodic stripping voltammetry [16], so again the analytical applications have predominated. To date, theoretical studies have been confined to reversible electrode processes. Keller and Osteryoung [17] have considered differential pulse voltammetry at a hanging drop mercury electrode under slow scan rate conditions. Recently, Blutstein and Bond [18] considered the use of faster scan rates in differential pulse voltammetry to evaluate the  $i-E$  curve at a DME using a single drop of mercury. Subsequently, Rifkin and Evans [19] presented an equation for differential pulse voltammetry for a reversible electrode process which is more general than that of Keller and Osteryoung, but data were again reported only at moderately slow scan rates [20].

Thus, at the present point of time, developments in differential pulse voltammetry have been extremely limited. In particular, very conservative approaches have been adopted in terms of instrumentation, theory and methodology, compared with, say, a.c. techniques where a complete arsenal of approaches exist in all these directions [21–24]. In the present communication, a versatile computerized system for performing a wide range of differential pulse voltammetric experiments at scan rates at least an order of magnitude faster than previously possible has been developed. D.c. pulse and differential pulse components of the experiment can be extracted simultaneously, unlike existing instrumentation where only the differential pulse response is provided. The new technique of cyclic differential pulse voltammetry is also described and the use of variable d.c. scan rates in differential pulse voltammetry as a means of studying the nature of the measurement in terms of both the d.c. and pulse components of the experiment is considered. Future studies will be directed towards providing a quantitative account of the theory for the different approaches developed.

## EXPERIMENTAL

### (I) *Reagents and preparation*

The solutions  $1.0 \times 10^{-3} M K_3Cr(CN)_6/1.0 M KCN$ ,  $1.0 \times 10^{-3} M CdCl_2/1.0 M KCl$  (pH 3), and  $1.5 \times 10^{-4} M (NH_4)_2S/0.1 M NH_4OH$  were prepared in distilled, deionized, and filtered water. Commercially available reagent grade compounds were used, with the exception of  $K_3Cr(CN)_6$ , which was synthesized according to the method of Christensen [25]. Nitrogen was used to remove oxygen from the solutions. The solution  $1.0 \times 10^{-3} M$  9,10-diphenylanthracene (DPA)/0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile was prepared by vacuum line techniques [26]. Burdick and Jackson spectroscopic grade acetonitrile was dried by repeated trap-to-trap distillation over  $P_2O_5$ , with the time of contact in the early stages kept brief to prevent polymerization. A vacuum cell containing the DPA and TBAP was kept under vacuum for 24 h before the acetonitrile was added by distilling it into a specially built side-arm of the cell. The solution was degassed by repeated freeze-pump-thaw cycles until the pressure during the pump cycle was below  $10^{-3}$  Torr. The DPA was Aldrich gold label and the TBAP was Southwest Analytical polarographic grade. The TBAP was dried in a vacuum oven at  $95^\circ C$  for 72 h and stored in a vacuum desiccator over  $P_2O_5$  prior to use.

### (II) *Electrochemical cells*

The aqueous work was carried out in a Metrohm cell using a Princeton Applied Research Corporation micrometer head hanging mercury drop working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl (saturated NaCl) reference electrode. The vacuum cell use for non-aqueous work contained a working electrode made from a 28 gauge platinum wire sealed in a soft glass tube which was then cut and polished perpendicularly to the wire. The tube was sealed to a Pyrex support with Torr Seal epoxy. This provides a surface area of approximately  $8.0 \times 10^{-4} cm^2$ . The auxiliary electrode was a coaxially coiled platinum wire and the reference was a quasi-reference electrode formed by isolating a small sample of the bulk solution in a separate cell with a platinum electrode and an asbestos fiber leak terminating as close to the working electrode as possible. The entire cell was assembled with ground glass joints, minimally greased with Dow Corning silicone high vacuum grease. It is described in considerably greater detail elsewhere [26].

All data were obtained at the ambient temperature of  $25 \pm 0.2^\circ C$ .

### (III) *Electronics*

The Raytheon Data Systems RDS-500 computer was used to perform the experiments. Potentiostat control input was provided by the 16-bit,  $153 \mu V$  resolution Datel 169B digital-to-analog converter, driven over optically isolated lines to reduce noise transmission from the computer. Current follower output was monitored by the 14-bit, 1.22 mV resolution Raytheon analog-to-digital converter in the AID system, using the sample-and-hold input circuit. Timing

was regulated by the interrupt-connected programmable real-time clock. A conventional three-electrode potentiostat with positive feedback was used to control the cells. It was constructed with Analog Devices 45J 10 MHz operational amplifiers, which were operated with damping capacitors. For pulse measurements, where it was necessary to measure small currents following large peaks, a variable gain clipping circuit was placed between the current follower output and the analog-to-digital converter input. This gave a considerably improved signal-to-noise ratio. It was constructed around a 48J Analog Devices amplifier, which has an unusually short overload recovery time. A Tektronix 475 oscilloscope monitored the current signal and was used to adjust the positive feedback to give the sharpest current response to a step possible without oscillation. It was also used to verify that the clipping circuit did not distort the data.

#### (IV) Programming

Two different programs were used for these experiments: *CYCLIC* for cyclic staircase voltammetry and *DCYCLIC* for differential pulse cyclic voltammetry. They are both based on GAADS (Generalized Acquisition, Analysis, and Display System), a flexible set of routines developed at Northwestern University to simplify real-time control and data processing in electrochemical and spectroscopic experimentation. Coding is in SYM II, the Raytheon assembly language. They are capable of displaying data in a wide variety of formats on either a Tektronix 611 storage oscilloscope or a Complot DP-1 digital plotter, and results can be stored on a 9-track magnetic tape library for future processing.

One cycle of a sample potentiostat control signal from *CYCLIC* is shown in Fig. 1, along with a detail of one staircase potential increment illustrating the

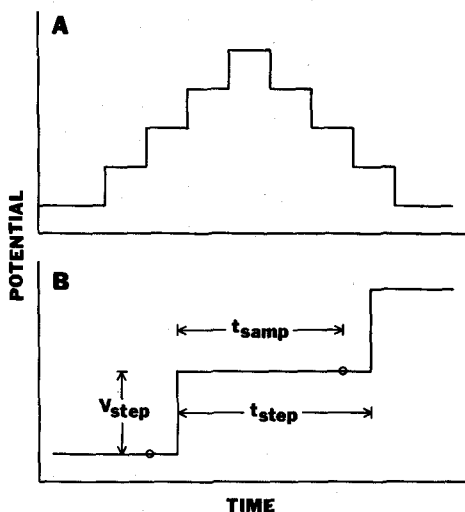


Fig. 1. Potentiostat control signal output for cyclic staircase voltammetry, from program *CYCLIC*. (A) shows one complete cycle and (B) shows a detail of one potential increment with the timing and potential parameters illustrated. The small circles in (B) indicate the times at which the current is sampled.

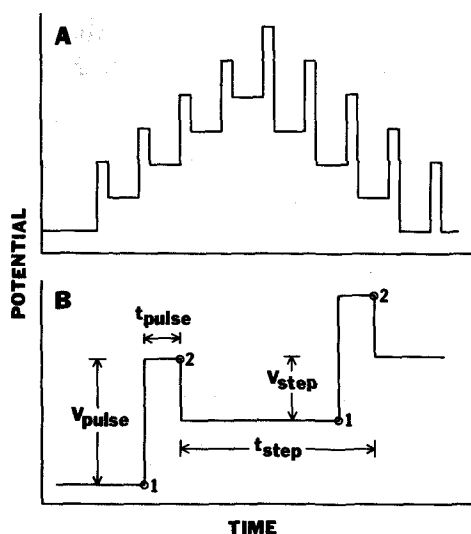


Fig. 2. Potentiostat control signal output for cyclic pulse differential staircase voltammetry, from program DCYCLIC. (A) shows one complete cycle and (B) shows a detail of one potential increment with the timing and potential parameters illustrated. The small numbered circles in (B) indicate the two times during a single increment that the current is sampled.

definitions of the timing and potential parameters. Similar data for the differential pulse cyclic program DCYCLIC, are presented in Fig. 2. All parameters shown, as well as the initial potential and scan limits, may be set to any reasonable value with simple commands entered on the teletype, subject to a lower clock interval limit of  $200 \mu s$  and the DAC resolution of  $153 \mu V$ . However,  $t_{step}$  is set indirectly by specifying the scan rate,  $v(V_{step}/t_{step})$ . In DCYCLIC, the pulse height ( $V_{pulse}$ ) may be of either sign, but it does not change with scan direction, and the current is plotted against the potential prior to the pulse.

It should be noted that DCYCLIC measures the current at two times during a single staircase potential: immediately before ( $i_1$ ) and at the end ( $i_2$ ) of the pulse. Normally  $i_2 - i_1$  (differential pulse response) is displayed, but either  $i_1$  (staircase response) or  $i_2$  (pulse response) may be displayed separately. For the version of DCYCLIC used to take the data in this communication, only one response can be chosen for a single scan, since only one is stored; however, the program can easily be changed to store and display all three types of data simultaneously.

The programs can record several cycles, either storing them individually or averaging them together. Recording can be delayed until several cycles have been generated so that the system can reach a steady state before averaging starts. This noise reduction technique has not been used on the data presented in this communication so that the basic noise characteristics of the system can be fairly evaluated.

#### THEORETICAL CONSIDERATIONS

From Fig. 2 the dual nature of the differential pulse cyclic experiment is readily revealed. Measurement of the current before the pulses is equivalent to

the staircase voltammogram, providing that the ratio of step width,  $t_{\text{step}}$ , to pulse width,  $t_{\text{pulse}}$ , is sufficient for the influence of the preceding pulse to have decayed to zero.

In accordance with the theory of staircase voltammetry, the current before the pulse will be dependent on the scan rate,  $v$ . For example, with a reversible process of the kind



and for very short step widths and very small increments of potential, the current will increase proportionally to  $v^{1/2}$ . It must be recognized that the measurement of current in the presence of the pulse also contains a d.c. term which will show the same scan rate dependence. Subtraction of the current in the presence and absence of the pulse will clearly not null out the d.c. term because it is being measured at a different time in the d.c. response. The influence of the d.c. distortion term has been examined in detail under polarographic conditions [27] and it has been shown experimentally that distortion becomes significant at short drop times [28]. Under voltammetric conditions an analogous d.c. faradaic distortion should also be present, but since the d.c. component and therefore the distortion is scan rate dependent, this may not have been noticed in previous work where very slow scan rates were employed. Furthermore, without measuring the magnitude of the d.c. terms, as is undertaken in this work, their influence on the curves obtained could easily be overlooked. In the present work the upper limit of scan rate that could be used without distortion is an important feature to be examined.

If the electrode process is fully reversible on both the pulse and d.c. time scales with both species soluble, and the pulse is of the same sign in both scan directions, then an extension of the theory presented by Rifkin and Evans [19,20] can be used to predict overlap of the curves from the forward and reverse scans in the slow scan limit and the results should be independent of scan rate. However, if the process is reversible but amalgam formation is involved at the hanging mercury drop electrode:



then the sphericity of amalgam formation alters the surface concentrations, modifying the d.c. terms, especially in the reverse scan direction. As concluded from the work of Beyerlein and Nicholson [29], this will cause the peak height in the reverse direction of the differential pulse cyclic to be greater than that from the forward scan and a scan rate dependence will be introduced.

Knowledge of the d.c. cyclic behavior rapidly enables a qualitative estimation of the differential pulse behavior. Quasi-reversible charge transfer, for example, will lead to separation of the peaks in the forward and reverse scan directions and peak heights of unequal magnitude. An irreversible following chemical reaction with reversible charge transfer will result in a smaller peak height for the reverse scan than for the forward scan.

Each of the effects considered above is very important; however, a detailed quantitative theoretical study of them is beyond the scope of this work. Nevertheless, it should be obvious that once a complete theoretical study of differential pulse voltammetry is provided, it will provide a powerful addition to the

techniques available for quantitative studies of electrode kinetics and diagnosis of electrode reaction mechanisms.

## RESULTS AND DISCUSSION

The compound 9,10-diphenylanthracene (DPA) can be both oxidized and reduced at a platinum electrode in acetonitrile [30,31]:



where  $k_s$  is the heterogeneous charge transfer rate constant. Figure 3 shows a staircase cyclic voltammogram of the electrode processes and both waves can be seen to be extremely well defined.

Figure 4 shows the cyclic differential pulse voltammogram taken at the same d.c. scan rate, potential range, and potential increment used in Fig. 3. The pulse width employed was 200  $\mu\text{s}$ , compared with a step time of 1 ms. The scan rate of greater than  $1 \text{ V s}^{-1}$  is approximately two orders of magnitude faster than those usually encountered in differential pulse voltammetry, but excellent data are still obtained. Note, also, that the resolution and nature of the differential pulse cyclic peaks, in terms of ease of measurement of their height and position, are far superior to that obtained in staircase voltammetry. The height of the peaks for the reduction process is smaller than that for the oxidation, which almost certainly reflects the fact that  $k_{s1}$  is less than  $k_{s2}$ , a feature that is not readily discernible from the staircase cyclics. Undoubtedly, the differential pulse cyclic technique will have considerable advantages in studies of electrode kinetics and a detailed investigation of the theory for this class of electrode process is currently being pursued.

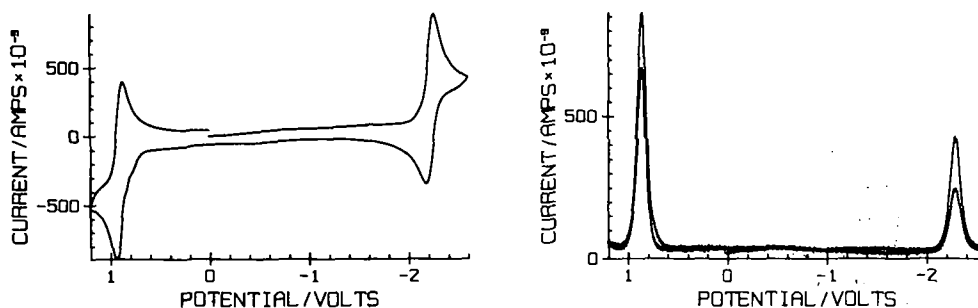


Fig. 3. Cyclic staircase voltammogram of  $1.0 \times 10^{-3} \text{ M}$  DPA/0.1 M TBAP in acetonitrile. Parameters:  $\nu = 1.07 \text{ V s}^{-1}$ ,  $V_{\text{step}} = 1.07 \text{ mV}$ ,  $t_{\text{step}} = t_{\text{samp}} = 1.00 \text{ ms}$ . Initial potential is 0.000 V and the initial scan direction is cathodic.

Fig. 4. Cyclic differential pulse staircase voltammogram of  $1.0 \times 10^{-3} \text{ M}$  DPA/0.1 M TBAP in acetonitrile. Parameters:  $\nu = 1.07 \text{ V s}^{-1}$ ,  $V_{\text{step}} = 1.07 \text{ mV}$ ,  $t_{\text{step}} = 1.00 \text{ ms}$ ,  $V_{\text{pulse}} = 10.1 \text{ mV}$ ,  $t_{\text{pulse}} = 0.200 \text{ ms}$ . The initial potential is 0.000 V and the initial scan direction is cathodic.

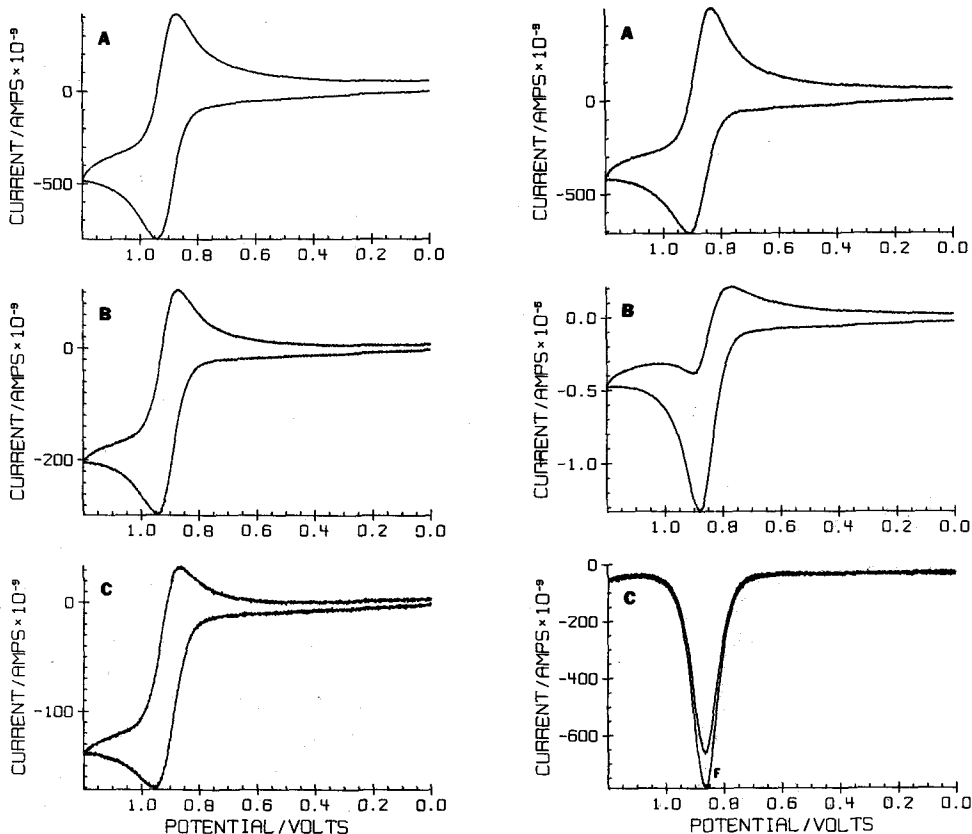


Fig. 5. Cyclic staircase voltammograms for oxidation of  $1.0 \times 10^{-3} M$  DPA/0.1 M TBAP in acetonitrile. Parameters: (A)  $v = 1.07 \text{ V s}^{-1}$ ,  $t_{\text{step}} = t_{\text{samp}} = 1.00 \text{ ms}$ , (B)  $v = 0.101 \text{ V s}^{-1}$ ,  $t_{\text{step}} = t_{\text{samp}} = 10.6 \text{ ms}$ , (C)  $v = 0.0200 \text{ V s}^{-1}$ ,  $t_{\text{step}} = t_{\text{samp}} = 53.4 \text{ ms}$ . For all,  $V_{\text{step}} = 1.07 \text{ mV}$ , the initial potential is 0.000 V and the initial scan direction is anodic.

Fig. 6. Cyclic differential pulse staircase voltammograms for oxidation of  $1.0 \times 10^{-3} M$  DPA/0.1 M TBAP in acetonitrile. Parameters:  $v = 1.07 \text{ V s}^{-1}$ ,  $V_{\text{step}} = 1.07 \text{ mV}$ ,  $t_{\text{step}} = 1.00 \text{ ms}$ ,  $V_{\text{pulse}} = 10.1 \text{ mV}$ ,  $t_{\text{pulse}} = 0.200 \text{ ms}$ . The initial potential is 0.000 V and the initial scan direction is anodic. (A) is the staircase response, (B) is the pulse response, and (C) is the differential pulse response. The "F" indicates the forward scan.

Figure 5 shows a staircase cyclic voltammogram of the oxidation process at various scan rates and, as expected, the magnitude of the d.c. current decreases quite substantially as the scan rate decreases. The same series of voltammograms for the reductive process are virtually identical except for the sign of the current. The increased noise level associated with the curves obtained at lower scan rates results predominantly from the fact that fewer analog-to-digital converter bits are being used when measuring the smaller current signal.

Figures 6a and 6b show the individual components of the pulse and staircase experiment at a scan rate of about  $1 \text{ V s}^{-1}$  for the oxidative process which, via subtraction, constitute the differential pulse curve seen in Fig. 6c. The equivalence of Figs. 5a and 6a shows that the staircase voltammogram can indeed be recorded in the presence of the pulse. From Fig. 6b it is also apparent that



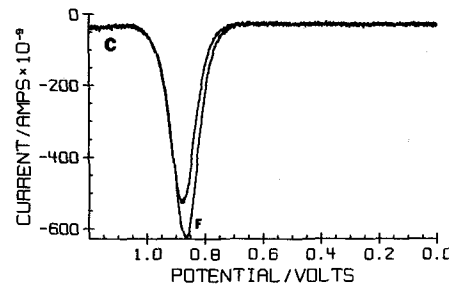
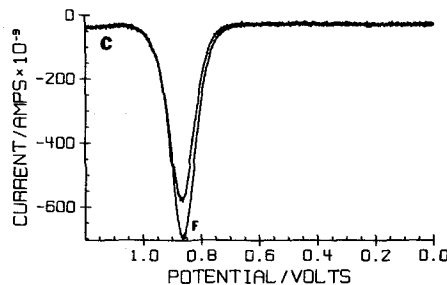
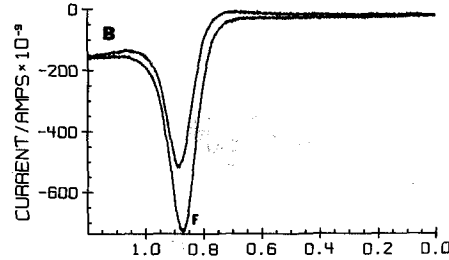
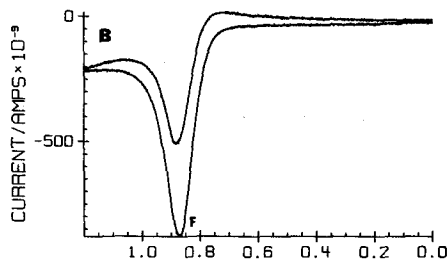
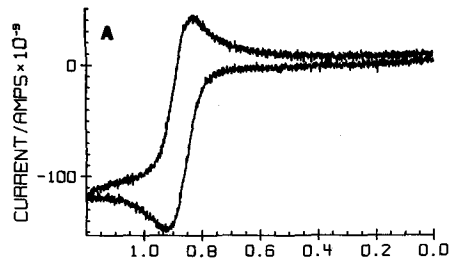
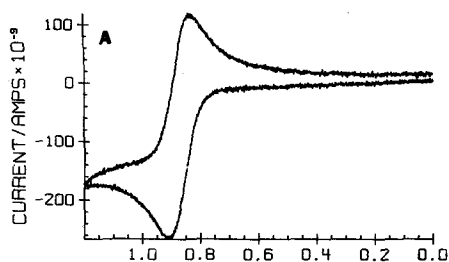


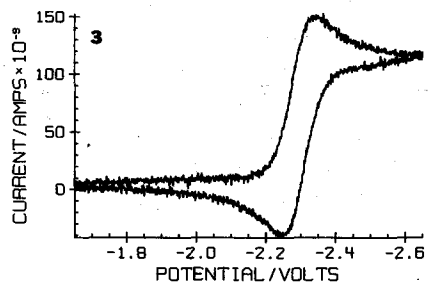
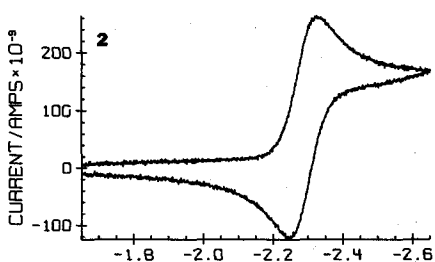
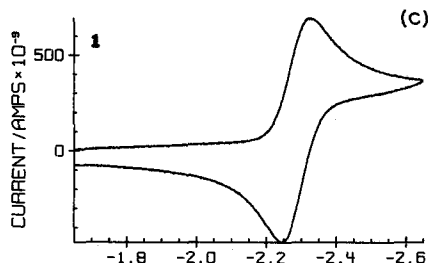
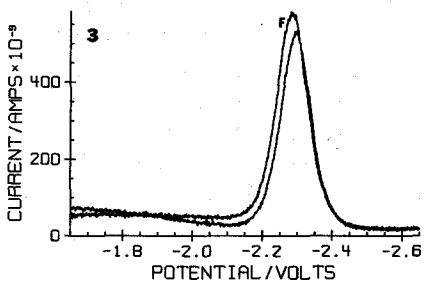
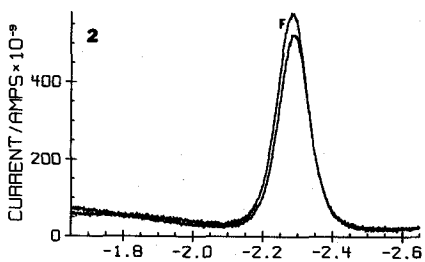
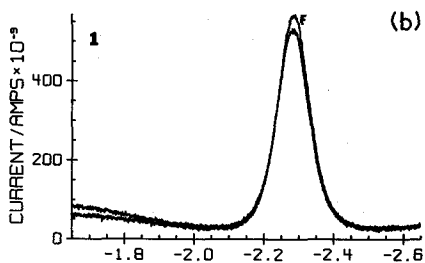
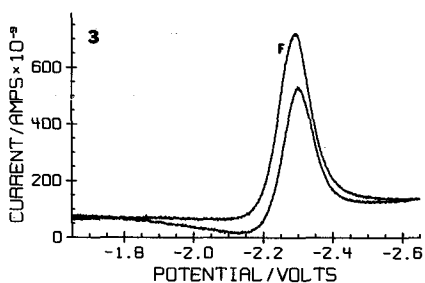
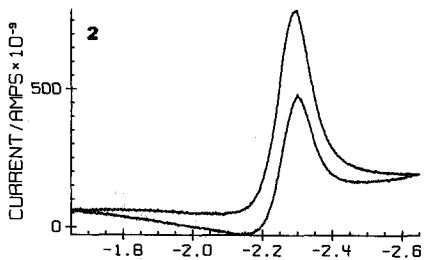
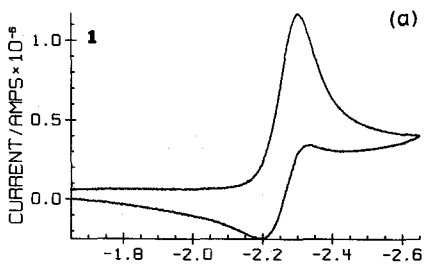
Fig. 7. Same as Fig. 6 except:  $v = 0.101 \text{ V s}^{-1}$ ,  $t_{\text{step}} = 10.6 \text{ ms}$ .

Fig. 8. Same as Fig. 6 except:  $v = 0.0200 \text{ V s}^{-1}$ ,  $t_{\text{step}} = 53.4 \text{ ms}$ .

the d.c. contribution in the pulse experiment is a significant term at fast scan rates because the staircase cyclic response resulting from the d.c. terms is clearly evident. As shown in Fig. 6c, the subtraction process almost eliminates the d.c. terms for this close to reversible electrode process; however, a small residual effect does remain. As explained earlier, the imperfect subtraction occurs because the d.c. component in Fig. 6b is measured at a slightly different time than that in Fig. 6a.

Figures 7a–c show the same series of curves for the oxidative step at a slower d.c. scan rate, and clearly the pulse response appears to be a function of scan rate, changing as the magnitude of the d.c. terms decreases. In Figs. 8a–c at even slower scan rate, the pulse and differential pulse curves are in the process of gradually becoming equivalent, as the d.c. component becomes even smaller. The pure pulse curve can, in fact, be shown experimentally to be independent of scan rate and the apparent distortion and scan rate dependence in the differential pulse results at fast scan rates is entirely due to the d.c. terms.

In previous discussion, the reduction process in the DPA system was considered to be less reversible than that for oxidation because, as shown in Fig. 4, a smaller differential pulse current was obtained. The d.c. terms for both elec-



trode processes have already been shown to be essentially identical in magnitude, which implies that the relative importance of the d.c. contribution should be enhanced when studying the reduction of this compound. Figure 9a shows the pulse response at various scan rates and Fig. 9b the differential pulse scans. Note the far greater baseline inequivalences on either side of the peaks in the forward and reverse scans, compared with the oxidation wave. Clearly, if d.c. terms were completely subtracted out, then the baselines on either side of the differential pulse curve would be zero. Examination of Fig. 9c shows that the currents from the staircase cyclic voltammograms are non-zero and far from equivalent in both forward and reverse directions at potentials far removed from the peak and because the d.c. terms are significant in magnitude relative to the pulse term for this electrode process, they are evident in the measured differential pulse response at fast scan rates. A non-zero baseline problem must arise for all concentrations of the electroactive species and will become more significant for slower  $k_s$  values or at faster scan rates.

The reduction of  $\text{Cr}(\text{CN})_6^{3-}$  in 1 M KCN at mercury



has a  $k_s$  value of about  $0.4 \text{ cm s}^{-1}$  [32] and is therefore close to reversible. A series of experiments were recorded on this system with the results shown in Figs. 10 and 11. The pulse amplitude has the opposite sign from that used in the previous reduction. At low scan rates (Fig. 11) the d.c. terms are relatively unimportant, and the expected response for a reversible process is seen, but at scan rates of  $1 \text{ V s}^{-1}$  again some d.c. distortion is evident, in that curves do not overlap in forward and reverse scan directions.

The reduction of cadmium in chloride media at mercury



has a  $k_s$  value greater than or equal to  $1 \text{ cm s}^{-1}$  [33] and is essentially reversible. Figure 12 shows the scan rate dependence of this system. Despite the fact that the d.c. terms are quite large (Fig. 13), very little d.c. distortion is found even with a scan rate of  $1 \text{ V s}^{-1}$  for this essentially reversible system and the pulse and differential pulse curves are nearly identical. It should be noted that for this system the height of the reverse scan is greatly enhanced at slower scan rates because of amalgam formation, as is clearly seen in Fig. 12. The additional information contained in the reverse sweep is clearly demonstrated. Most of the work reported in the literature on amalgam systems has been undertaken at

Fig. 9a. Pulse response from cyclic differential pulse staircase voltammograms for reduction of  $1.0 \times 10^{-3} \text{ M DPA}/0.1 \text{ M TBAP}$  in acetonitrile. Parameters: (1)  $v = 1.07 \text{ V s}^{-1}$ ,  $t_{\text{step}} = 1.00 \text{ ms}$ , (2)  $v = 0.101 \text{ V s}^{-1}$ ,  $t_{\text{step}} = 10.6 \text{ ms}$ , (3)  $v = 0.0200 \text{ V s}^{-1}$ ,  $t_{\text{step}} = 53.4 \text{ ms}$ . For all,  $V_{\text{step}} = 1.07 \text{ mV}$ ,  $V_{\text{pulse}} = -10.1 \text{ mV}$ , and  $t_{\text{pulse}} = 0.200 \text{ ms}$ . The initial potential is  $-1.650 \text{ V}$  and the initial scan direction is cathodic. The "F" indicates the forward scan.

Fig. 9b. Same as Fig. 9a except the differential pulse responses are shown.

Fig. 9c. Same as Fig. 9a except the staircase responses are shown.

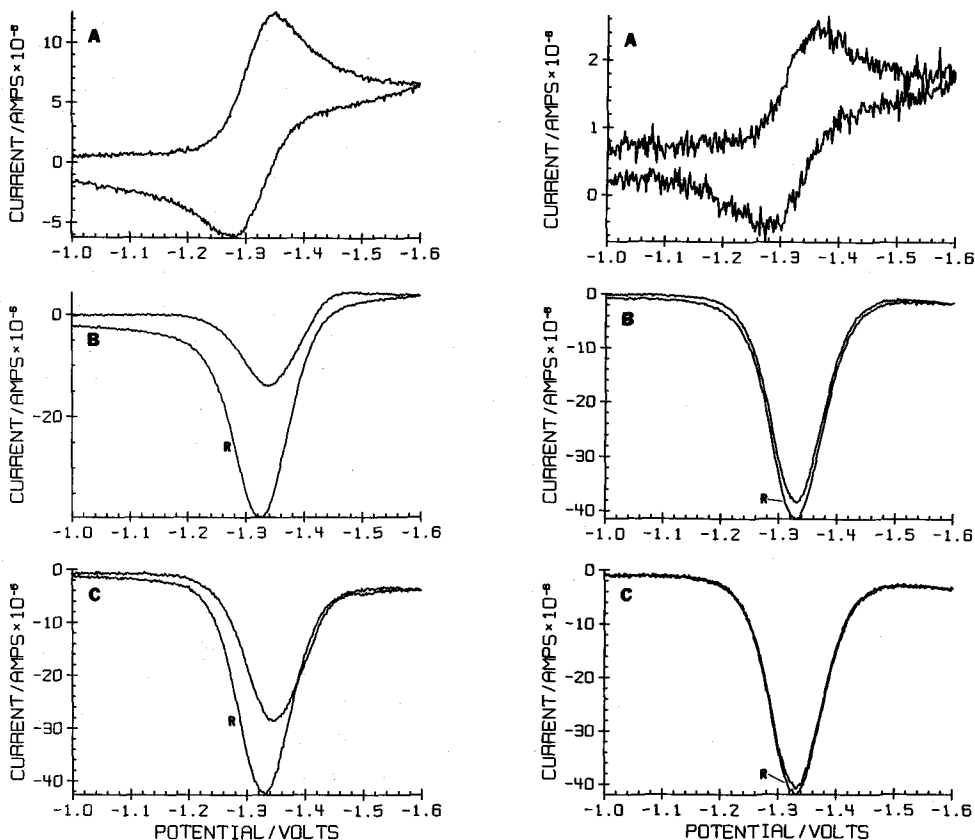


Fig. 10. Cyclic differential pulse staircase voltammograms for reduction of aqueous  $1.0 \times 10^{-3} M K_3Cr(CN)_6/1.0 M KCN$ . Parameters:  $\nu = 0.992 V s^{-1}$ ,  $V_{step} = 1.98 mV$ ,  $t_{step} = 2.00 ms$ ,  $V_{pulse} = 25.0 mV$ ,  $t_{pulse} = 0.0200 ms$ . The initial potential is  $-1.000 V$  and the initial scan direction is negative. (A) is the staircase response, (B) is the pulse response, and (C) is the differential pulse response. The "R" indicates the reverse scan direction.

Fig. 11. Same as Fig. 10 except:  $\nu = 0.200 V s^{-1}$  and  $t_{step} = 99.2 ms$ .

scan rates less than  $10 mV s^{-1}$ , so it is clear, from these data, that the d.c. terms were unimportant in the measured response.

One final example, the oxidation of mercury in the presence of sulfide ( $0.1 M NH_4OH$ )



and the subsequent stripping of insoluble  $HgS$  is considered to demonstrate how the present instrumentation can be used to advantage in simultaneously examining the d.c. and differential pulse cyclic responses. This electrode process has been studied by numerous workers [34,35]. It is extremely complex and it is therefore difficult to anticipate whether the staircase or differential pulse cyclic will provide the better analytical response. Figure 14 shows that in fact the staircase voltammograms are substantially simpler than the pulse cur-

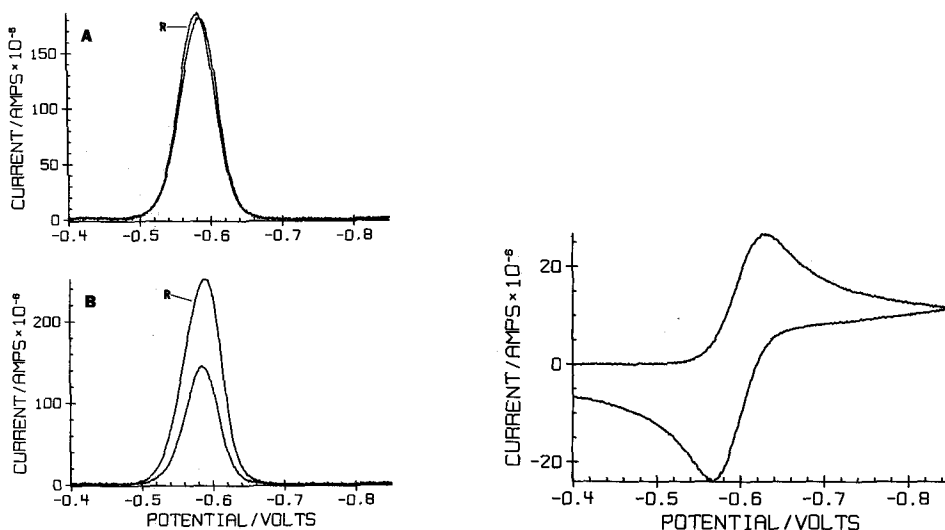


Fig. 12. Differential pulse response from cyclic differential pulse staircase voltammograms of aqueous  $1.0 \times 10^{-3} M$   $CdCl_2/1.0 M$   $KCl$  (pH 3). Parameters: (A)  $v = 1.07 V s^{-1}$ ,  $t_{step} = 1.00 ms$ , (B)  $v = 0.0200 V s^{-1}$ ,  $t_{step} = 53.4 ms$ . For both,  $V_{step} = 1.07 mV$ ,  $V_{pulse} = -25.0 mV$ ,  $t_{pulse} = 0.200 ms$ . The initial potential is  $-0.400 V$  and the initial scan direction is cathodic. The "R" indicates the reverse scan.

Fig. 13. Staircase response corresponding to Fig. 12a.

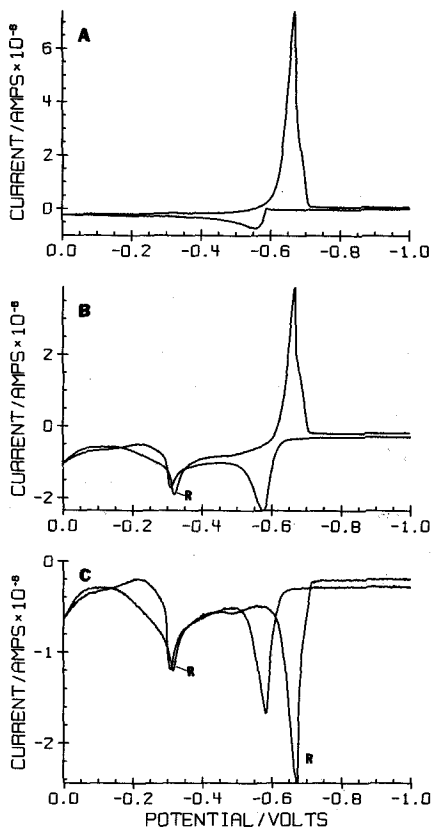


Fig. 14. Cyclic differential pulse staircase voltammograms of aqueous  $1.5 \times 10^{-4} M$   $(NH_4)_2S/0.1 M$   $NH_4OH$ . Parameters:  $v = 0.100 V s^{-1}$ ,  $V_{step} = 1.98 mV$ ,  $t_{step} = 19.8 ms$ ,  $V_{pulse} = 25 mV$ ,  $t_{pulse} = 0.200 ms$ . The initial potential is  $-1.000 V$  and the initial scan direction is anodic. (A) is the staircase response, (B) is the pulse response, and (C) is the differential pulse response. The "R" indicates the reverse scan.

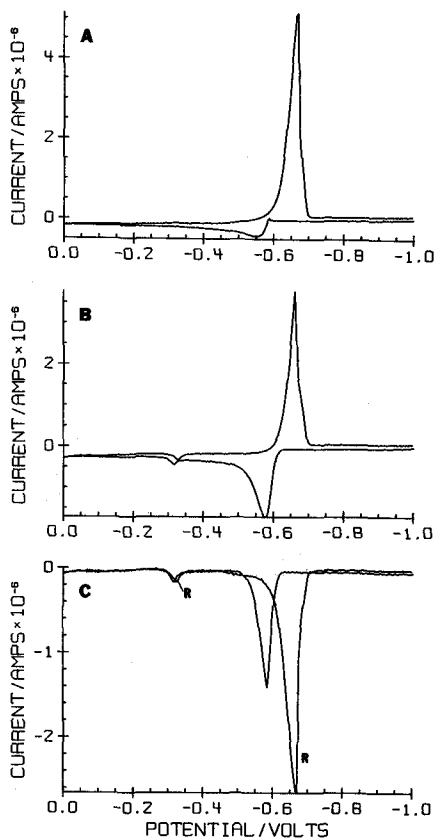


Fig. 15. Same as Fig. 14 except:  $V_{\text{step}} = 3.97$  mV,  $t_{\text{step}} = 39.6$  ms, and  $t_{\text{pulse}} = 8.00$  ms.

ves. The reverse sweep, corresponding to the reduction of insoluble mercury sulfide, shows considerable enhancement of current, but unlike previous cases, the current under staircase voltammetric conditions is much larger than the pulse or differential pulse currents. Under cathodic stripping conditions for the determination of sulfide, there is no doubt that differential pulse voltammetry is not the preferred technique. The additional peaks and complexity observed obviously arise from the application of the pulse. As expected, increasing the pulse width (Fig. 15) does provide some improvement in the differential pulse curves; however, the use of the wider pulse necessarily restricts the scan rate that can be used, and since time saving is a likely motivation for implementing the technique, the staircase method is still to be preferred.

## CONCLUSIONS

Instrumentation capable of performing both the usual and cyclic forms of fast scan differential pulse voltammetry and simultaneously recording the pulse and staircase responses should prove extremely valuable in studies of fundamental electrode processes and in analytical work. However, scan rates faster than  $1 \text{ V s}^{-1}$  do not seem advisable because of d.c. distortion, particularly in

irreversible systems. Furthermore, if scan rates faster than this are used, pulse widths have to be decreased below 100  $\mu\text{s}$  and construction of instrumentation with such capabilities becomes a demanding task. Such rates also imply that significant charging current distortion (in addition to d.c. faradaic distortion) will contribute to the observed responses. In the present work, the currents were measured near the end of the duration of the pulse and staircase potentials, and it was assumed that the  $RC$  nature of the cell and the  $IR$  compensation of the potentiostat were such that the charging current terms were almost negligible. Such an assumption would not be valid when examining dilute solutions at scan rates in excess of  $1\text{ V s}^{-1}$  and employing pulse widths of less than 100  $\mu\text{s}$  duration unless an exceedingly fast, powerful, and stable potentiostat were used.

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