Pulse Voltammetric Methods of Analysis [and Discussion]

R. A. Osteryoung, Janet Osteryoung, W. J. Albery and G. T. Rogers

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ELECTROANALYTICAL

Pulse voltammetric methods of analysis

By R. A. Osteryoung and Janet Osteryoung
Department of Chemistry, State University of New York at Buffalo,
Buffalo, New York 14214, *U.S.A.*

The techniques of normal and differential pulse voltammetry are presented together with equations describing these techniques. A number of specific applications for both differential and normal pulse, including determination of As^{III} in sewage and the determination of sulphide, are presented. Advantages of amperometric titrations in eliminating 'background' errors are shown, with the titration of Cu^{II} with EDTA as a specific example. The use of square-wave voltammetry, a new, rapid-pulse technique, is presented, and an application in which this technique is employed in an electrochemical high performance chromatographic detector used for nitrosamine analysis is discussed.

Introduction

Analytical chemistry is of great importance in almost all aspects of industry. This article is devoted to one very small facet of that area, namely pulsed electrochemical methods. It is worth pointing out that electrochemistry in the United States in an academic setting is, for the most part, carried out by those who bear the title of analytical chemist. This is more of a historical accident than anything else, since a great deal of academic electrochemistry developed as a result of the work of Heyrovsky on polarography, and was carried out in the early years by individuals who, in an academic setting, were considered to be analytical chemists (Laitinen & Ewing 1977).

Normal and differential pulse voltammetry

In what follows we point out two facets of pulse voltammetry: (1) the analytical utility of these techniques and (2) the application of these techniques to elucidation of mechanisms of electrode reactions that might lead to the development of industrial processes. Our own research in electrochemistry is concerned with technique development and the application of these techniques to realistic analytical problems. We shall cover here aspects of past work and indicate present and future directions for work in pulse voltammetry.

The parent of modern pulse electroanalytical methods is Dr Geoffrey Barker, whose pioneering work at Harwell in the 1950s yielded pulse polarography (Barker & Gardner 1958). It is worth pointing out, before going into detail, that for widespread application of any analytical technique, instrumentation must be developed. In the late 1950s a pulse polarographic instrument, based on Barker's design, was manufactured in England and sold, at least in the United States, for about $25000; a princely sum in those days.

Figure 1 shows the wave forms applied in modern pulse voltammetry, applied to either a mercury or solid electrode. In the so-called 'normal' pulse (n.p.) mode, millisecond pulses of successively increasing amplitude are applied to an electrode; if the dropping mercury electrode

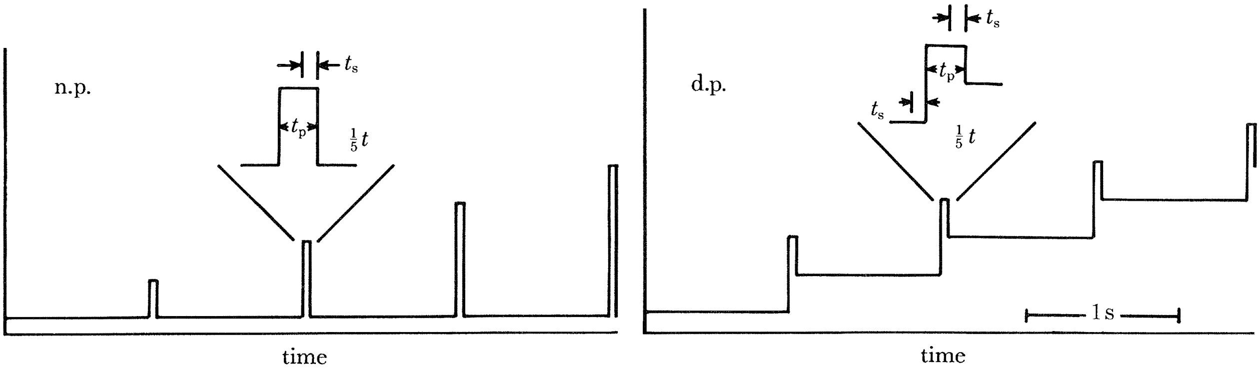

FIGURE 1. The potential–time waveforms for normal pulse (n.p.) and differential pulse (d.p.) voltammetry.

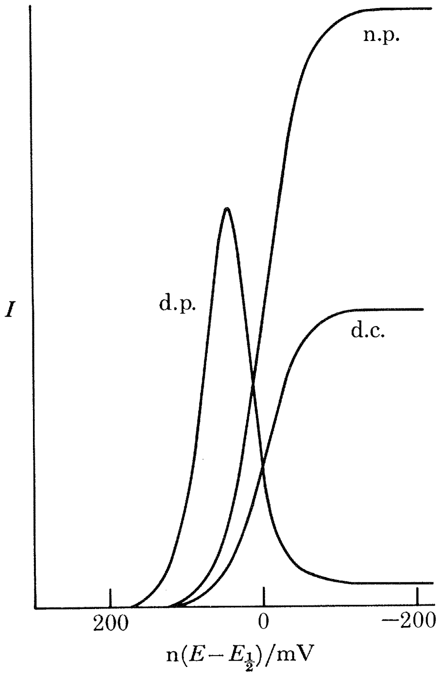

FIGURE 2. Current–potential response in d.c., n.p., and d.p. polarography.

is used, a pulse is applied at some fixed time during the drop growth to ensure that the area of the drop is constant from pulse to pulse. The initial potential is such that no reaction can take place. The current is measured at some fixed time, usually at the end of pulse application. At some potential, depending on what is in solution, a current flows as a result of a faradaic process, say the reduction of a simple metal ion. The technique is, in our jargon, sampled-current single-potential step chronoamperometry.

In the differential pulse (d.p.) mode (again let us refer to a dropping mercury electrode) the potential is moved slightly between each drop (the drops are knocked off mechanically) and a pulse of constant amplitude is applied, again for a few milliseconds. The period between these pulses can be 1–10 s. The current is measured immediately before and at some fixed time after pulse application. The difference in current is recorded.

The shape of the current–potential response curves that one obtains is shown in figure 2, which compares the response for regular d.c. polarography and n.p. and d.p. polarography. The limiting current plateau in the d.c. and n.p. techniques is directly proportional to the concentration of the ion that has diffused to, and reacted at, the electrode surface. The peak current in d.p. polarography is also proportional to the concentration of the material in solution reacting at the electrode surface. The shapes of the waves in the d.c. and n.p. techniques are much the same; note that since the magnitude of the current in the n.p. mode is almost 10 times greater than that for d.c. polarography, the analytical sensitivity is that much greater. The d.p. curve has the shape of the derivative of the d.c. or n.p. curve. The peak current in d.p. polarography is somewhat less than the limiting current in n.p. polarography. Thus, both pulse methods offer markedly increased sensitivity over regular d.c. polarography. A few equations seem called for at this point.

The shape of the current–potential curve for the reversible reduction of O to R in single potential step chronoamperometry is given by the well known Cottrell equation

$$i = nFAD_{\mathrm{O}}^{\frac{1}{2}}C_{\mathrm{O}}^{\mathrm{b}}/(\pi t_{\mathrm{p}})^{\frac{1}{2}}\ (1+\zeta\theta), \tag{1}$$

where i is the current at a given potential (microamps); n is the number of electrons transferred per mole of the oxidized form O; F is the Faraday constant (96485 C mol^{-1}); A the electrode area (square centimetres); D_{O} the diffusion coefficient of O (square centimetres per second); $C_{\mathrm{O}}^{\mathrm{b}}$ the bulk concentration of O (millimoles per litre); t_{p} the time of current measurement (seconds), nominally the pulse width of figure 1; $\zeta = (D_{\mathrm{O}}/D_{\mathrm{R}})^{\frac{1}{2}}$, where D_{R} is the diffusion coefficient of the reduced form (square centimetres per second); and $\theta = \exp\ (nF(E-E^{\circ})/RT)$, where E is the potential (volts), E° the standard potential for reduction of O to R (volts), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T the absolute temperature (kelvins). When E is much more negative than E°, $\theta \approx 0$ and the limiting current,

$$i = nFAD_{\mathrm{O}}^{\frac{1}{2}}C_{\mathrm{O}}^{\mathrm{b}}/(\pi t_{\mathrm{p}})^{\frac{1}{2}}, \tag{2}$$

is attained. The equation for the limiting current for n.p. polarography is obtained by using the appropriate equation for the drop area as a function of time:

$$\begin{aligned} \mathrm{A} &= 4\pi\ (3/4\pi\rho)^{\frac{2}{3}}\ (mt_{\mathrm{d}})^{\frac{2}{3}} \\ &= 8.49 \times 10^{-3}(mt_{\mathrm{d}})^{\frac{2}{3}}, \end{aligned} \tag{3}$$

where ρ is the density of mercury (13594 mg cm^{-3} at 25 °C), m the flow rate of mercury (milligrams per second) and t_{d} the age of the drop (seconds). Combining (2) and (3), the limiting current, $i_{\mathrm{n.p.}}$, in n.p. polarography is given by

$$i_{\mathrm{n.p.}} = 463nD_{\mathrm{O}}^{\frac{1}{2}}\ m^{\frac{2}{3}}\ t_{\mathrm{d}}^{\frac{2}{3}}\ C_{\mathrm{O}}^{\mathrm{b}}/t_{\mathrm{p}}^{\frac{1}{2}}. \tag{4}$$

In d.c. polarography, the times t_{d} and t_{p} are the same. In addition, the growth of the drop into undepleted regions of solution causes the current to be $(\frac{7}{3})^{\frac{1}{2}}$ as large as for a stationary electrode. As a result the limiting current, $i_{\mathrm{d.c.}}$, from (2) and (3) becomes

$$i_{\mathrm{d.c.}} = 708nD_{\mathrm{O}}^{\frac{1}{2}}m^{\frac{2}{3}}t_{\mathrm{d}}^{\frac{1}{6}}C_{\mathrm{O}}^{\mathrm{b}}. \tag{5}$$

In the d.p. mode the differential with respect to potential of (1) yields the peak current

$$i_{\mathrm{d.p.}} = i_{\mathrm{n.p.}}\ (1-\sigma)/(1+\sigma), \tag{6}$$

where $\sigma = \exp\,(nf\Delta E/2RT)$ and ΔE (volts) is the height of the pulse of constant amplitude shown in figure 1.

Notice that in each case the current is directly proportional to concentration and that the proportionality is given by a simple equation. Furthermore in both n.p. and d.p. the signal depends on $t_p^{-\frac{1}{2}}$. Thus decreasing the measurement time increases the sensitivity markedly.

Specific numbers might be helpful; detection limits for d.c. polarography are normally about 10^{-5} M in the species reacting at the electrode; for n.p. polarography the detection limit is about 10^{-6} to 10^{-7} M under favourable conditions. For d.p. polarography, the detection limits are of the order of 10^{-8} M. The reason for this may not be immediately evident; the actual peak current in d.p. (equation (6)) is less than the limiting current in n.p. (equation (4)). In other words, under comparable conditions, the sensitivity for n.p. is greater than for d.p. However, in all electroanalytical methods – in all analytical methods, in fact – one must consider the noise or background signal. Without going into any detail, we simply state that the noise or background level in the d.p. mode is almost two orders of magnitude less than in the n.p. or d.c. polarographic modes, and it is this decrease in background that increases the signal/noise ratio of the peak current in d.p. and therefore produces a lower detection limit.

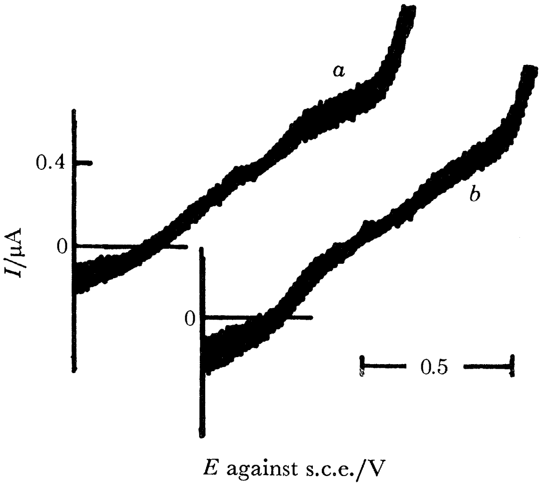

FIGURE 3. The d.c. polarographic reduction of As^{III}: (a) 1 M H_2SO_4; (b) 1 M HCl. [As^{III}] = 2×10^{-5} M; scan rate 10 mV s^{-1}; initial potential, –120 mV against saturated calomel dectrode (s.c.e.); drop time, 0.5 s.

APPLICATIONS

We illustrate the use of d.p. polarography with a practial application (Myers & Osteryoung 1973). Figure 3 shows the d.c. polarographic wave for the reduction of As^{III} in (a) 1 M sulphuric acid and (b) 1 M hydrochloric acid. If one examines the literature, d.c. polarography for As^{III} employs 1 M sulphuric acid as the medium of choice. However, remembering that the d.p. mode essentially examines the derivative of the d.c. curve, for d.p. work, 1 M HCl is much superior. D.p. polarograms of As^{III} in 1 M H_2SO_4 and 1 M HCl are shown in figure 4. HCl is clearly a better medium than H_2SO_4; in fact 1 M HCl is the medium of choice. In figure 5 we see a d.p. polarogram of As^{III} at about the 3×10^{-7} M level; the lower curve is 'background' i.e., the signal that one observes even in the absence of the faradaic reaction. It is the 'noise' referred to above. The curve on the right shows the effect of adding a small amount of surfactant to the

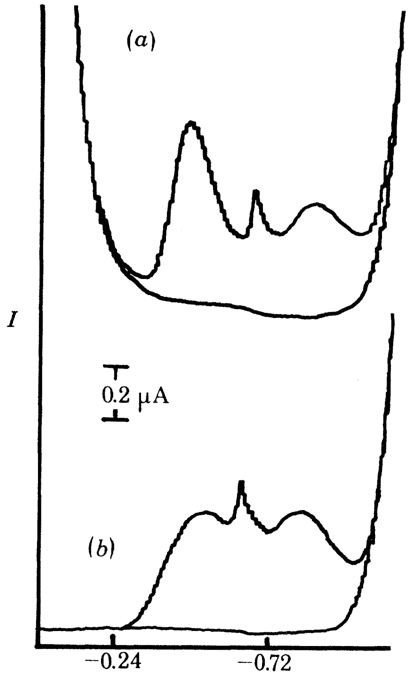

FIGURE 4. d.p. polarography of As^{III}: (*a*) 1 M HCl; (*b*) 1 M H_2SO_4. [As^{III}] = 8 μM; scan rate, 5 mV s^{-1}; drop time, 2 s; pulse amplitude, 50 mV.

solution, thereby dramatically altering the shape of both the background and the d.p. peak. Calibration curves for As^{III} are linear over better than four orders of magnitude (10^{-4} to 10^{-8} M).

The calibration curve for a solution containing a surfactant is also linear, but its slope (sensitivity) is less than for the solution with no surfactant. Certain electrochemical reactions of analytical interest are very sensitive to trace impurities of surfactants. However, as long as the impurity level remains quite constant, determinations can be carried out. The procedure developed here was employed for the determination of As^{III} in sewage by one of us (J.O.) and collaborators, who were interested in the rate at which a bacterium, *Pseudomonas fluorescens*, converts As^{III} to As^{V}. Analyses were carried out in samples of activated sludge, diluted 1 : 10 with 1.1 M HCl, broth cultures of *Alcaligenes faecalis*, broth cultures of *P. fluorescens* and other demanding sample types with measurement error of 2.3 μg l^{-1} As^{III} in the 100–500 μg l^{-1} range (Myers *et al.* 1973).

Next we turn to an example of the application of n.p. polarography. The reaction of sulphide at a mercury electrode should give rise to the formation of HgS(s). D.c. polarography, however, gives a variety of ill-defined waves. D.p. polarography is perhaps worse (figure 6). N.p. polarography, as shown in figure 6, gives exactly what theory predicts. A calibration curve is linear over several orders of magnitude (10^{-3} to 10^{-6} M). What causes this difference in response? The reaction of sulphide results in the formation of a film of HgS(s) at the electrode surface, and since mercury is a liquid, this can result in patches of HgS(s) on the surface, which give rise to turbulence at the drop surface. In the n.p. mode, because most time is spent at a potential where no reaction occurs (see figure 1), the amount of material reacting – the amount of HgS(s) actually formed at the electrode surface – is very small, and therefore the behaviour is

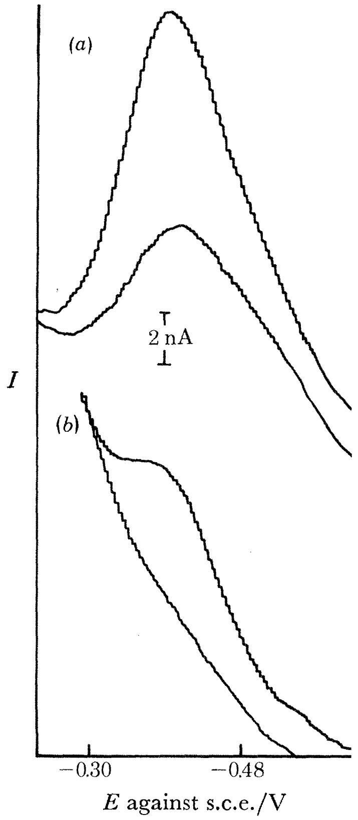

FIGURE 5. d.p. polarography of As^{III} in HCl, showing the effect of surfactant on faradaic and background currents. (*a*) 1 M HCl with (upper curve) and without (lower curve) 0.27 μM As^{III}. (*b*) As (*a*), with the addition of Triton X-100 at 10 μl/l. Scan rate, 2 mV s^{-1}; drop time, 2 s; pulse amplitude, 100 mV.

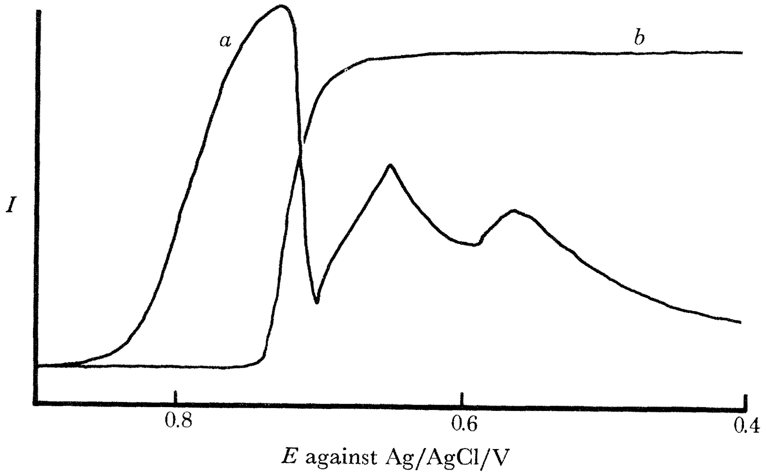

FIGURE 6. d.p. (*a*) and n.p. (*b*) polarograms for sulphide in sodium carbonate solution at a dropping mercury electrode. (*b*) 5 × 10^{-4} M Na_2S in 1 M Na_2CO_3; electrode area, 0.028 cm^2; t_p = 50 ms. (*a*) 1.6 × 10^{-3} M Na_2S in 1 M Na_2CO_3; t_p = 33 ms, ΔE = 50 mV.

ideal. This observation is the basis for an analytical method for sulphide that achieves detection limits on the order of 1 μM (Turner *et al.* 1975) and therefore is competitive with methods based on ion-selective electrodes.

AMPEROMETRIC TITRATIONS

As evidenced by figure 5, the background can have a considerable structure. To measure the peak height, which one does to obtain the magnitude of the analytical signal, it is necessary to know the baseline, i.e. the background in the absence of the electroactive material. In a real

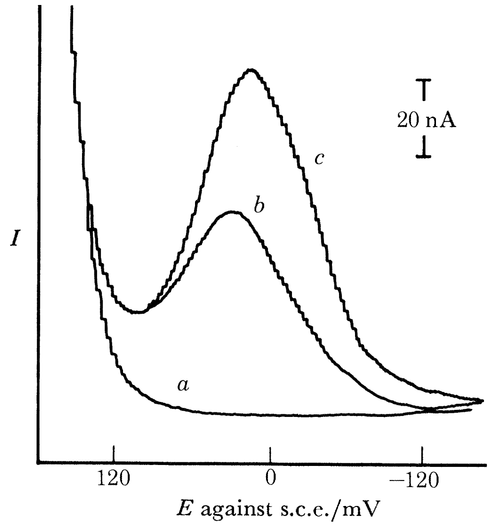

FIGURE 7. d.p. polarograms showing background interference with the Cu^{II} reduction wave due to Triton X-100. (*a*) 0.1 KNO_3 adjusted to pH 4.2 with HOAc. (*b*) As (*a*), but with Triton X-100 (10 μl/l) added. (*c*) As (*b*), but 2 μM in Cu^{II}. Scan rate, 2 mV s^{-1}; drop time, 2 s; pulse amplitude, 100 mV.

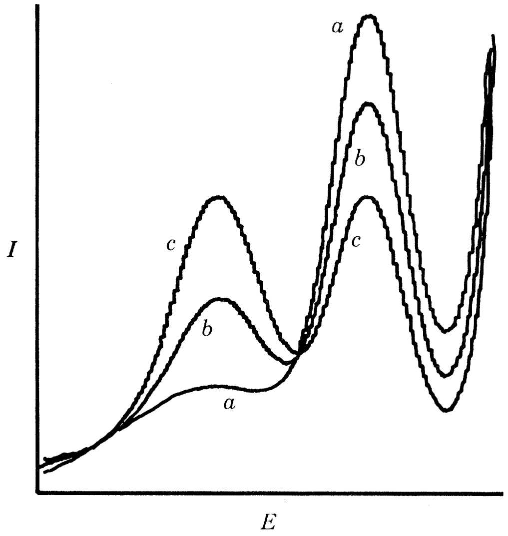

FIGURE 8. d.p. polarograms for the reduction of 2×10^{-5} M Cu^{II} in 0.1 M NH_4NO_3, pH 8. (*a*) 500 nmol Cu^{II}; (*b*) as (*a*), with 100 nmol EDTA; (*c*) as (*a*), with 200 nmol EDTA. Drop time, 0.5 s, ΔE = 100 mV; initial potential, − 150 mV against s.c.e.

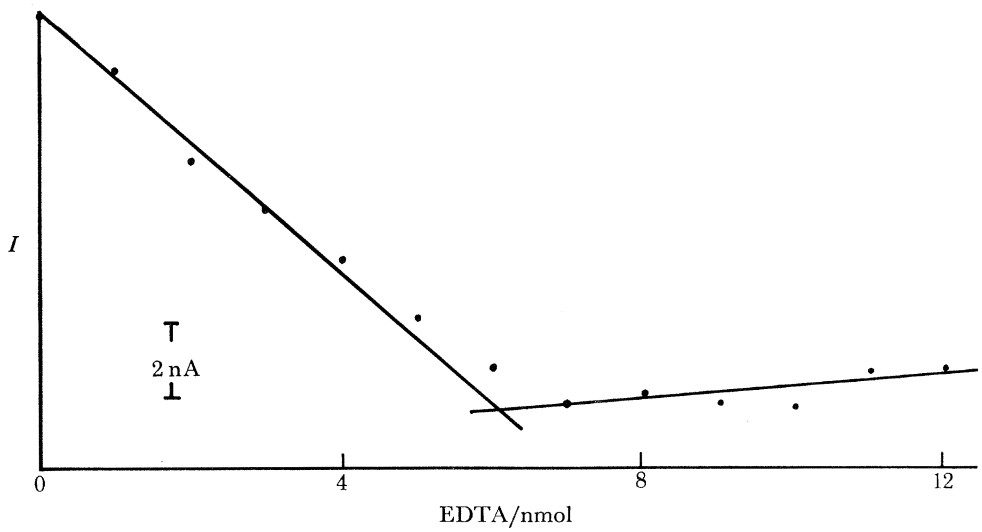

FIGURE 9. Typical titration curve for 5 nmol Cu^{II} (*ca.* 0.2 μM): 0.01 M KNO_3 adjusted to pH 4.2 with HOAc. Drop time, 2 s; initial potential, −20 mV against s.c.e.; pulse amplitude, 100 mV (anodic-going pulses).

sample the baseline is often unobtainable experimentally and is estimated by drawing the best straight line under the peak. This can clearly result in error (see figure 5*a*). A spectacular example of this problem is shown in figure 7, which displays the effect of surfactant on the background current at the potential for reduction of Cu^{II}. One way out of this is to perform amperometric titrations, in which the pulse voltammetric peak current is measured repetitively after the addition of a reagent. The chemical basis for an amperometric titration for Cu^{II} that avoids the background problem is shown in figure 8. D.p. polarograms are given for the reduction of Cu^{II} with added amounts of EDTA, which forms a complex with Cu^{II}. The equilibrium between free Cu^{II} and the copper–EDTA complex is slow, so one wave is seen for the reduction of the free Cu^{II} and another for the Cu–EDTA complex. By monitoring the free copper wave as a function of the amount of EDTA added, a curve similar to that in figure 9 is obtained. This represents a titration at about the 0.2 μM level, and is of about 5 nm of Cu^{II} (Myers & Osteryoung, 1974). Such techniques can be automated readily. We have recently carried out work on the simultaneous determination of Ca and Mg with such a titration, in which we observe the wave due to the reaction of the EDTA (or other chelons) at a mercury electrode to form a Hg–EDTA complex (Jackson *et al.* 1980). Such a titration is both more accurate and more sensitive than the conventional colorimetric titration procedures and could be readily automated.

INSTRUMENTATION

It is worth pointing out that the leap that has taken place over the past 15 years or so in the use of these pulse methods was a result of the introduction of reliable, inexpensive instrumentation. In about 1970, Princeton Applied Research Corporation, in the U.S.A., introduced its model 174 Polarographic Analyzer. At the time the instrument cost about $2000 (it is now double that in price); it was highly reliable and offered at very low cost the great sensitivity that the methods, originally devised by Barker, had promised. Since then many companies have produced similar instruments. Our own work has made use of both commercial instrumentation and minicomputers. The latter are used with suitable interfacing in an interactive way to provide experimental control and data acquisition and processing in real time. The purpose is to study and develop new pulse methods.

SQUARE-WAVE VOLTAMMETRY

One of the newer methods, again an outgrowth of work performed by Barker (1958), is what we have termed square-wave voltammetry. The waveform for this method is shown in figure 10. Again, referring to a dropping mercury electrode, although the technique is applicable to solid electrodes as well, a drop is permitted to grow for a fixed period of time, and then the wave form, which is a combination of a staircase and square wave, is applied. The complete voltage range is scanned during the life of one drop (a few seconds). A current measurement is made

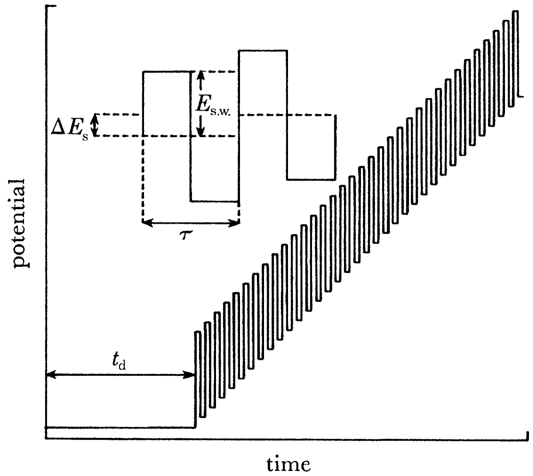

FIGURE 10. The square wave waveform. $E_{s.w.}$ is the square wave amplitude, ΔE_s the step height, τ the square wave period, and t_d the delay time at the initial potential before the initiation of the scan.

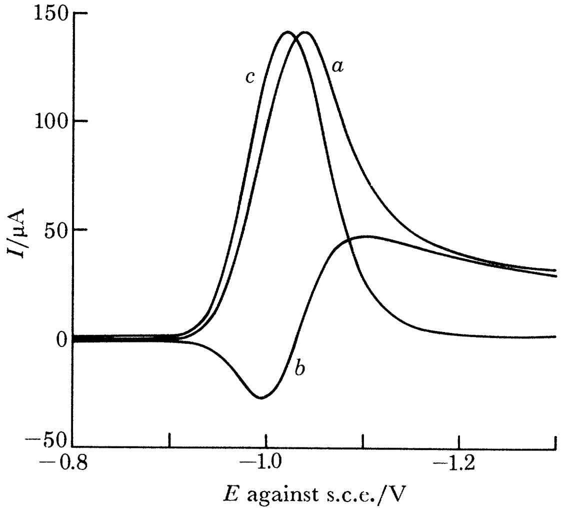

FIGURE 11. Square-wave voltammogram of 0.52 mM Zn^{II} in 0.1 M KNO_3; $\tau = 2$ ms, $\Delta E = 5$ mV, $E_{s.w.} = 25$ mV. (*a*) forward current, (*b*) reverse current, (*c*) net current.

during the forward-going pulse, and a second measurement is made during the reverse pulse. The current output is the forward current minus the reverse current (much as in d.p. polarography). The theory is rather complex (Christie *et al.* 1977), but the general features of the current–potential response are illustrated by the experimental results shown in figure 11. The forward current is that for reduction of Zn^{II} to the amalgam, and the reverse current is that for the reoxidation of the product amalgam to Zn^{II}. The difference current appears to be, and is theoretically, very similar to that obtained in the d.p. mode. Parenthetically it is worth noting that the individual forward and reverse currents plotted on the same potential scale resemble a cyclic voltammogram and in this case show clearly the irreversibility of the system.

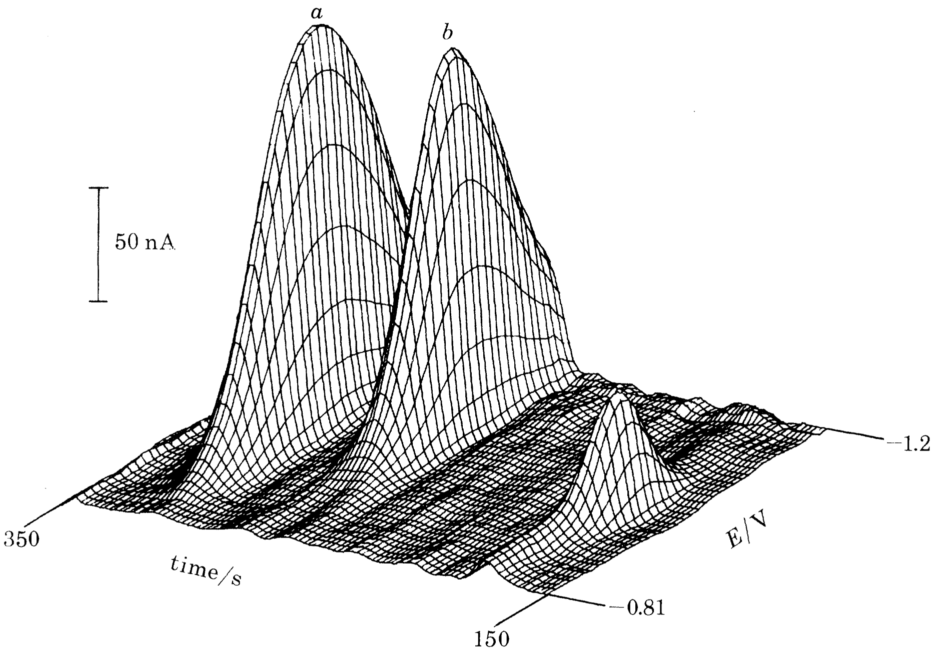

FIGURE 12. Three-dimensional chromatopolarogram of (*a*) *N*-nitrosodiethanolamine and (*b*) *N*-nitrosoproline. Concentration, 1×10^{-5} M; step height, 10 mV; square wave amplitude, 25 mV; square wave frequency, 100 Hz; mobile phase, 1% phosphate (pH 3.5). Background current has been subtracted.

Square-wave polarography can be employed both for analytical work and for detailed studies of the kinetics of electrode reactions and mechanisms. A calibration curve for the reduction of Cd^{II} has a dynamic range of *ca.* 10^{-8} to 10^{-3} M.

We have carried out most of our work on square-wave polarography with the use of a computer. Obviously, even though the price of computers, and microcomputers, is diminishing, one does not necessarily wish to use such instruments. Therefore, once we had established the utility of and reasonable parameters for the square-wave technique, we constructed an analogue, stand-alone instrument. This was done in collaboration with Dr Chaim Yarnitsky (1980) of the Technion in Israel.

The square-wave technique has a great deal of potential as the basis for a selective, sensitive detector for high-pressure liquid chromatography. Such a detector would compete favourably with multiple-wavelength u.v. detectors, particularly for organic substances, that can be oxidized or reduced. Applications involving aqueous or polar solvents with high ionic strength as mobile phase are especially attractive. This technique has been applied to the determination of *N*-nitrosamines by using separation on a C-18 bonded column (10 μm particle size) with 1% phosphate, pH 3.5, as the mobile phase (Samuelsson & Osteryoung 1981). A typical square-wave chromatopolarogram is shown in figure 12 (Samuelsson *et al.* 1980). The potential range for each scan is about 400 mV, and with a step height of 10 mV and square-wave frequency of 100 Hz the scan rate is 1 V s^{-1}. Thus a complete scan is carried out in about 0.4 s. The cycle time in this experiment is 2 s and the chromatopolarogram is obtained from 102 consecutive scans. The ability to carry out a complete voltage scan on a timescale small in comparison with the elution time makes it possible to resolve electrochemically species not resolved chromatographically and also to use the value of the peak potential as information for qualitative identification of unknown analytes.

The use of electroanalytical methods in industry obviously depends on the availability of individuals knowledgeable in the area, the applicability of the method to solve a real problem, and the instrumentation available. While a number of instruments are available, it is clear that in the view of at least some organizations, continued growth will take place. The best evidence of this is that new multi-purpose, but primarily pulse-voltammetric instrumentation has just been introduced in the United States by I.B.M. Instruments, Inc. This appears to indicate that another commercial instrument organization believes that there is a market which will expand as new electroanalytical methods are developed, as new techniques are found, and as we find problems, such as in h.p.l.c. detector systems, where the coupling of the inherent sensitivity and relatively low cost of electroanalytical techniques with a variety of separation techniques proves beneficial.

We hope that by showing past work, current research and some idea of future direction, we have at least whetted your appetite to find out if electroanalytical chemistry can be used for your problem.

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Discussion

W. J. ALBERY (*Department of Chemistry, Imperial College, London SW7 2AY, U.K.*). As Professor Osteryoung has explained, in using differential pulse techniques one shifts from the flat limiting current to the steep part of the wave. This part of the wave is sensitive to the electrode kinetics. If one uses a solid electrode which is gradually poisoning, then the peak height will be reduced as the electrochemical rate constant decreases. We have therefore found in our work that a better estimation of concentration can be found by multiplying the peak height by the width of the peak. This product is almost independent of the electrochemical rate constant and therefore of the degree of poisoning.

R. A. Osteryoung. While Professor Albery's comments are most interesting, it is not clear that they are theoretically precise. Work by K. Aoki & J. Osteryoung (*J. electroanalyt. Chem.* **110**, 19 (1980)), shows, in figs 4 and 5, that the product discussed by Professor Albery, which may be estimated from these figures, may be a rather complex function of both the rate constant and the charge transfer coefficient. It would appear – and at this time we have not done detailed calculations – that in some instances Professor Albery's statement is reasonable but that care should be exercised in using the product of the peak height and the half-width in a quantitative manner. Obviously, under some circumstances it will work, but theory suggests that problems exist.

G. T. Rogers (*Materials Development Division A.E.R.E., Harwell, U.K.*). Professor Osteryoung has convincingly pointed out the advantages of differential pulse polarography for mechanistic studies of electrode reactions compared in particular with conventional cyclic voltammetry.

In practice, solid electrodes are almost always heterogeneous, often to the extent that there are different reactions going on at different points on the surface. The different reactions may, for example, arise because of differences in electrode structure or composition, non-uniformity of primary current distribution or a surface adsorption that is very highly potential dependent.

Would Professor Osteryoung say what are the limitations, if any, on the advantages of differential pulse polarography for mechanistic studies on such heterogeneous electrodes?

R. A. Osteryoung. I should say, first, that the use of differential pulse voltammetry for mechanistic studies on solid or mercury electrodes should be avoided. The information sought may well be contained in the peak height and shape, but obtaining quantitative information is very, very difficult. Our own work on simulation of differential pulse voltammograms in slow electron transfer indicated in what amounts to essentially a pathological case yields good results, but in general, the peak is rather insensitive. On the other hand, square-wave voltammetry, particularly when one observes what I have called the 'up' and 'down' current, does appear to be useful for mechanistic studies. However, while we hope that this method will be useful at solid electrodes, we have little information, except in one instance, and I suspect that since the problems of surface heterogeneity do exist, as Dr Rogers states, problems will be encountered. However, square-wave voltammetry should be a much more useful technique for such studies than differential pulse, simply because of the timescale over which the experiment can be done. It is our hope to explore some of these problems.