

ELECTROANALYTICAL APPLICATIONS OF PULSE POLAROGRAPHY AND VOLTAMMETRY

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DEDICATION

The authors are, respectively, the academic great-granddaughter, great-grandson, and grandson of Professor I.M. Kolthoff. It is fitting that we dedicate this paper to him ; without his pioneering electroanalytical chemistry, none of us would have been academically born.

ABSTRACT

Some recent developments in the applications of pulse polarography and pulse voltammetry are discussed, with emphasis on techniques which avoid problems associated with the capacitive background current in pulse polarography.

It has long been recognized that the lower limit of applicability of polarography as an analytical technique is that low concentration of analyte at which the faradaic signal becomes negligible with respect to the double layer charging background. This lower limit depends on a variety of factors, including the supporting electrolyte, the potential at which the wave occurs, and the drop time, but it is generally around 10^{-5} M (1).

In an effort to extend the polarographic technique to lower concentrations, Barker (2,3) developed two variants of polarography, both called pulse polarography. The less sensitive of these variants, called normal (or integral) pulse polarography, is essentially sampled chronoamperometry at the dropping mercury electrode. The essentials of this technique are as follows: The growing drop is held at some potential E_1 (typically chosen such that no faradaic current flows for the electrode reaction of interest) ; at some fixed time, τ , in the life of the drop, the potential is stepped to some different value E_2 . After a waiting time, δ , to allow the charging current resulting from the application of the potential step to decay to a negligible value, the current is measured. The next drop is held at the same value of E_1 for time τ , but is pulsed to a different value of E_2 and the current is again measured at the same time in the drop life. The synchronization of the potential step and the current measurement with the growth of the drop is normally accomplished by mechanically dislodging the drop after current measurement and timing τ from this event. The potential wave-form for normal pulse polarography is shown in Figure 1.

The normal pulse polarogram consists of a plot of $I(\delta)$ vs. E_2 and has the same shape as an ordinary polarogram. Because the potential is not stepped to the reaction potential until late in drop life, the faradaic current is larger than in ordinary polarography, but the charging current due to drop growth is the same.

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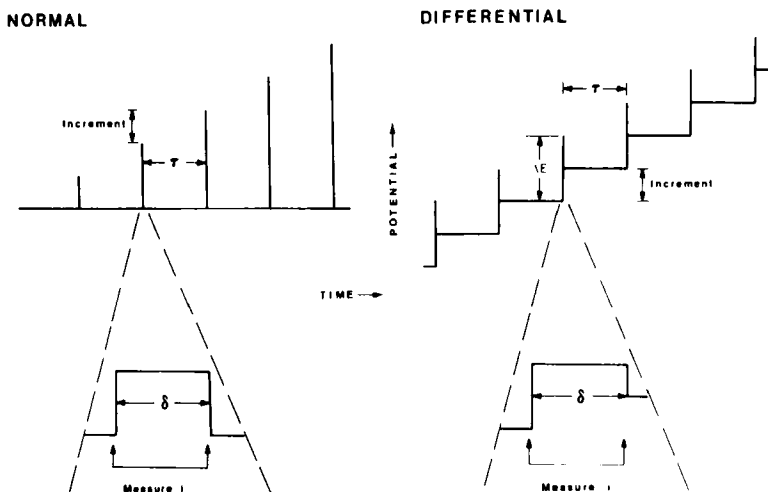


Figure 1. Schematic potential-time wave-forms for normal and differential pulse polarography.

The double layer charging contribution is minimized by the second of Barker's pulse techniques - differential pulse polarography. In this technique the potential E_1 is changed for each drop so that the amplitude of the potential step $\Delta E = E_2 - E_1$ is constant. This potential wave-form is also shown in Figure 1. The current is measured just before the step is applied and at time δ after application of the step. The difference between these currents is the output parameter. The faradaic current is of the same order of magnitude as in normal pulse polarography (4), but the capacitive background current is much less.

Figure 2 shows d.c., normal pulse, and differential pulse polarograms for 2×10^{-5} F Pb(II) in 1 F HCl. Comparison of curves C and D shows that the normal and differential pulse faradaic currents are of the same order of magnitude, while the background is much less in the differential mode. Comparison of curve D with curves A and B shows the enhancement of the faradaic response obtained in normal pulse polarography while the backgrounds are essentially the same. The observed difference in baselines is due to the presence of small amounts of faradaic impurities; in carefully purified and deoxygenated supporting electrolytes, the d.c. and normal pulse polarographic background curves are in fact identical.

It should be noted that the background curve for d.c. and normal pulse polarography have the form of a surface charge density vs. potential curve; the background in differential pulse polarography is smaller in absolute magnitude and has the form of a differential capacitance curve.

In many analytical problems, the existence of the non-faradaic background presents no problems; the background can be determined in a separate blank experiment. For other applications, such as the analysis of natural water samples, each sample is unique and a blank solution without the material of interest is not available. The analyst then has the problem of separating the faradaic response of the material of interest from the unknown background on

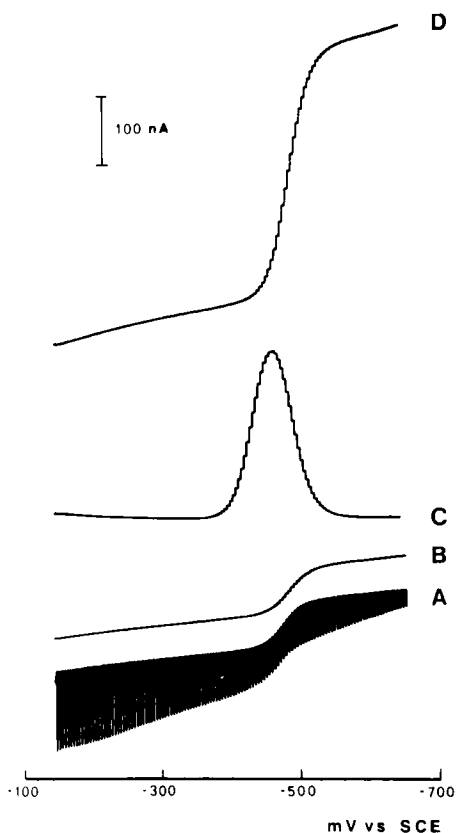


Figure 2. A. d.c., B. samples d.c., C. differential pulse ($\Delta E = -50$ mV), D. normal pulse polarograms for 2×10^{-5} F Pb(II) in 1 F HCl. $\delta = 30$ msec ; drop time = 2 sec ; scan rate = 2 mV/sec. Data obtained with modified Princeton Applied Research Model 174 Polarographic Analyzer.

which it is superimposed. The commonly-used method of standard additions is of no help in this regard since it corrects only for matrix effects in the slope, but not the intercept, of the analytical line. The use of standard additions implicitly assumes that the intercept of the calibration line is zero.

In our Laboratories, we have been concerned with development of pulse procedures which are applicable at trace levels and which do not have the problems associated with the non-faradaic background observed in pulse polarography at the dropping mercury electrode.

Perhaps the most straight-forward method of eliminating problems of the growing drop is to use a stationary electrode. Figure 3 shows a differential pulse voltammogram for 4 ng/ml Cd(II) obtained at a hanging mercury drop electrode (5). The background current shown in this figure is incompletely relaxed double layer charging current resulting from the potential steps ; the supporting electrolyte concentration is quite low and the potentiostat used in this early work had no provision for compensation of the iR drop in the solution.

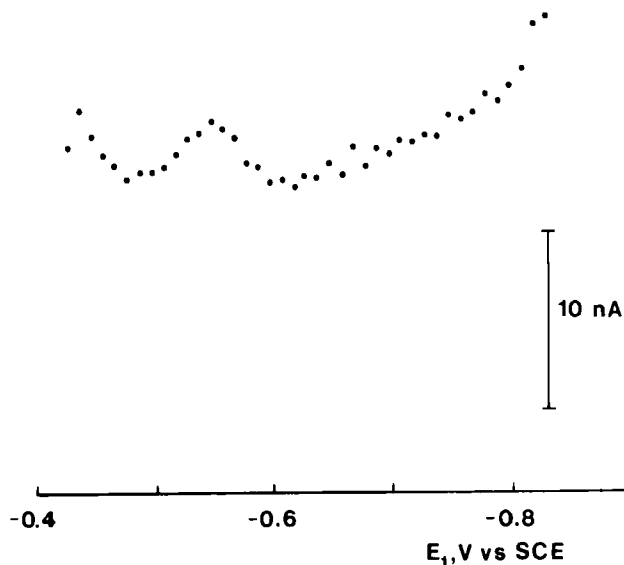


Figure 3. Differential pulse voltammogram of 4 ng/ml Cd(II) in 5×10^{-4} F KNO_3 .
Hanging mercury drop area = 0.0414 cm^2 ; $\Delta E = -50 \text{ mV}$; $\delta = 20 \text{ msec}$;
 $\tau = 0.2 \text{ sec}$. Each point is the average of 20 pulses.

We have also made extensive use of pulse voltammetric procedures in our study of molten salt electrochemistry (6-8). In the molten NaAlCl_4 solvent, in which the double layer capacitance of tungsten and carbon electrodes is quite high, cyclic voltammograms show a large double layer charging whereas pulse voltammetry, particularly in the normal mode, yields very clean and easily interpretable curves.

Linear scan stripping voltammetric curves also exhibit a large effect of double layer charging current. We have investigated differential pulse voltammetric stripping from the thin film mercury electrode in the expectation that the background currents would be greatly reduced (9-11). That this expectation was satisfied is demonstrated by the data in Figure 4. Not only is the background less in differential pulse stripping but the analytical sensitivity is also greater (10). This greater sensitivity allows the use of shorter plating times to obtain equivalent current response. Similar increase in sensitivity and decrease in background have been reported for stripping from the hanging mercury drop electrode (12).

Direct differential pulse polarography can be used even for unique samples at trace levels if the true background can be determined. One case in which this determination of the true background is possible is in the determination of arsenic(III) in 1 F HCl (13). After the total response for the sample has been determined, the As(III) is oxidized to the electroinactive As(V) by addition of an excess of Ce(IV) . The excess Ce(IV) is consumed by the Hg collected in the bottom of the polarographic cell, forming calomel. The background can then be determined by repeating the differential pulse polarographic scan. A calibration curve at very low levels obtained by this technique is shown in Figure 5. The detection limit calculated from the data in this figure is 0.2 ng As/ml at the 95% confidence level. Since the reduction of As(III) is electrochemically irreversible, both the slope and the intercept of the

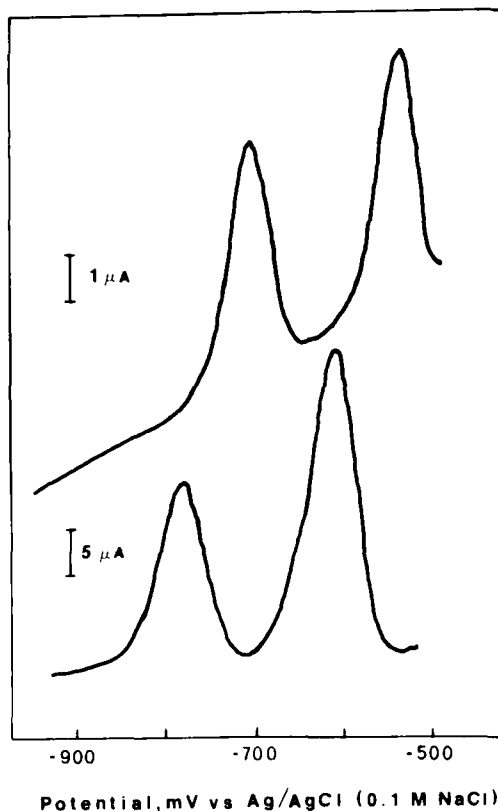


Figure 4. Comparison of linear scan and differential pulse stripping from the thin-film mercury electrode. Upper curve : linear scan, 200 mV/sec ; lower curve : differential pulse, $\Delta E = +100\text{mV}$; $\delta = 7 \text{ msec}$. Sample : urine spiked with 4 ng/ml Cd(II) and Pb(II).

calibration plot are affected by surfactants. At least one standard addition should be used to determine the slope of the analytical line, followed by oxidation of the As(III) and determination of the true background. This procedure has been used to determine As in very adverse matrices, such as unfiltered activated sludge from waste water treatment plants.

Another "standard subtraction" technique by which the background problems may be avoided is amperometric titration of the electroactive material. Figure 6 shows a differential pulse polarogram for Cu(II) in the presence of a surface-active material, Triton X-100. Clearly, direct determination of the Cu(II) concentration would be impossible without a knowledge of the true background current. Figure 7 shows that a differential pulse amperometric titration of the Cu(II) with EDTA yields accurate results, even at very low concentrations (14).

We have also developed some instrumental techniques which compensate for the capacitive background resulting from drop growth (15). The background in ordinary pulse polarography arises from the fact that the current is measured at two different times and at two different potentials in the life of each drop. Since the capacitive components of these two measured currents are different, the output difference current must contain a capacitive component.

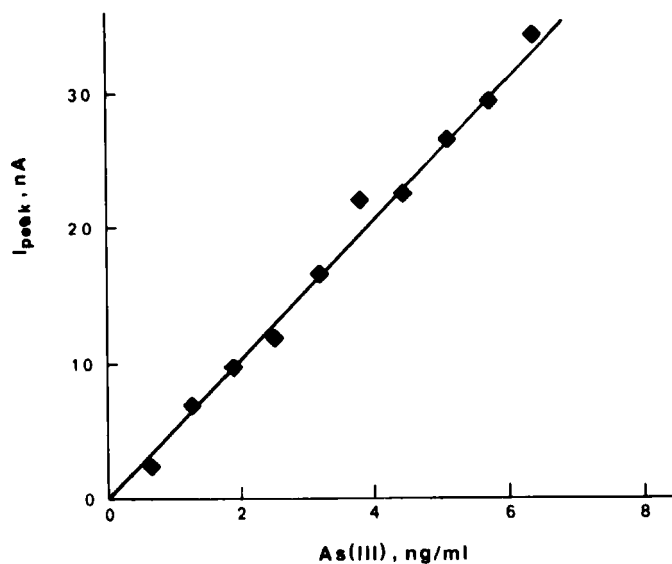


Figure 5. Differential pulse polarographic calibration curve for As(III) on 1 F HCl, using the background determination procedure described in text.

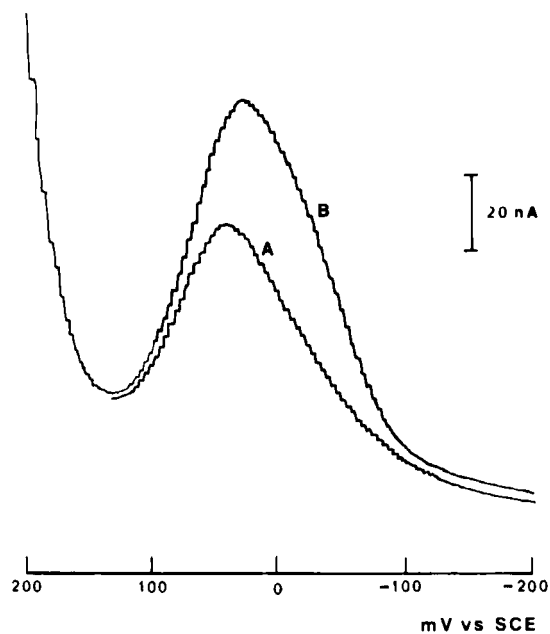


Figure 6. Differential pulse polarograms. A. 0.1 F KNO_3 (pH 4.2) plus 0.001% Triton X-100 ; B. same as A plus 2×10^{-6} F Cu(II).

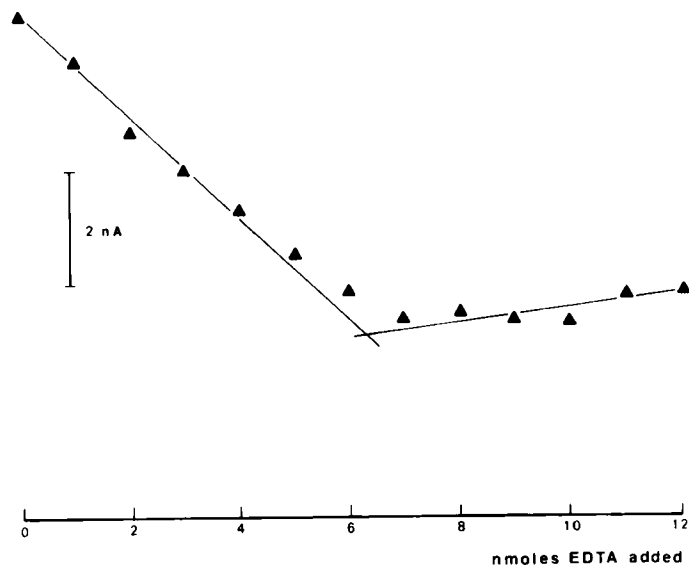


Figure 7. Differential pulse amperometric titration of Cu(II) with EDTA. Taken : 5.05 nmoles ; found : 6.25 nmoles ; reagent blank : 1.20 nmoles.

The effect of this capacitative component may be reduced by making only one measurement on each drop, always at the same potential and at the same time in drop life.

One technique which accomplishes compensation of the capacitative background is alternate drop pulse polarography (15). This variant technique derives its name from the fact that only alternate drops are pulsed from potential E_1 to E_2 ; the intervening drop remains at potential E_2 throughout its life. The output is the difference in current measured at time $\tau + \delta$ for the pulsed and the non-pulsed drops. The wave-forms and timing for alternate drop pulse polarography are shown in Figure 8.

It has been shown (15) that, for a reversible electrode reaction, the alternate drop pulse polarographic current has the same potential dependence as the ordinary pulse polarographic faradaic current, but is diminished in magnitude by the factor $(1 - \sqrt{7\delta/3(\tau + \delta)})$. An illustration of the efficacy of alternate drop differential pulse polarography in reducing the capacitative background is shown in Figure 9 (16).

An even simpler technique for dealing with the background problem is constant potential pulse polarography (15). The name derives from the characteristic that the value of E_2 is the same for all drops. The wave-form and timing are shown in Figure 10. This wave-form, which may be considered the inverse of the ordinary normal pulse wave-form, can be obtained by a very slight modification of a commercially available pulse polarograph (17). Only one current measurement is made per drop, at potential E_2 and time $\tau + \delta$; the output current as a function of E_1 is of the same form as a normal pulse polarogram, but superimposed on a constant capacitative background component. The diminution factor observed depends on the value of E_2 , relative to the half-wave potential, but is no smaller than the factor $1 - \sqrt{7\delta/3(\tau + \delta)}$. The decrease in the capacitative background observed in constant potential pulse polarography is illustrated in Figure 11.

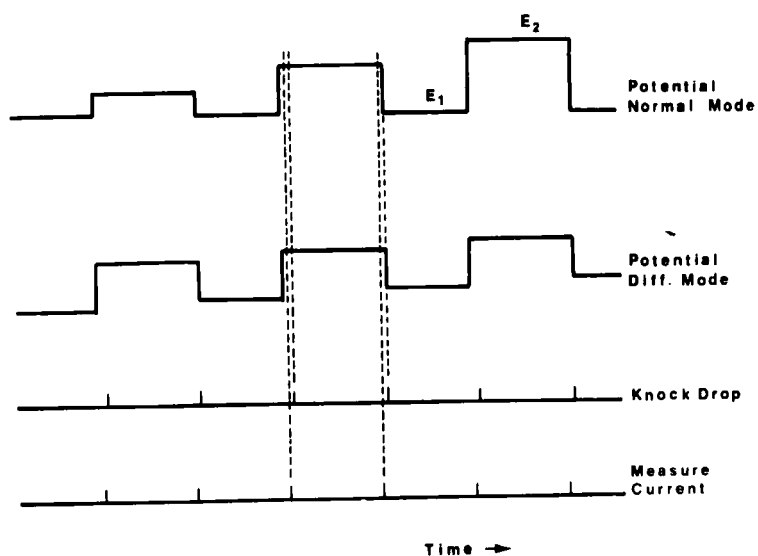


Figure 8. Schematic wave-forms and timing for alternate drop pulse polarography.

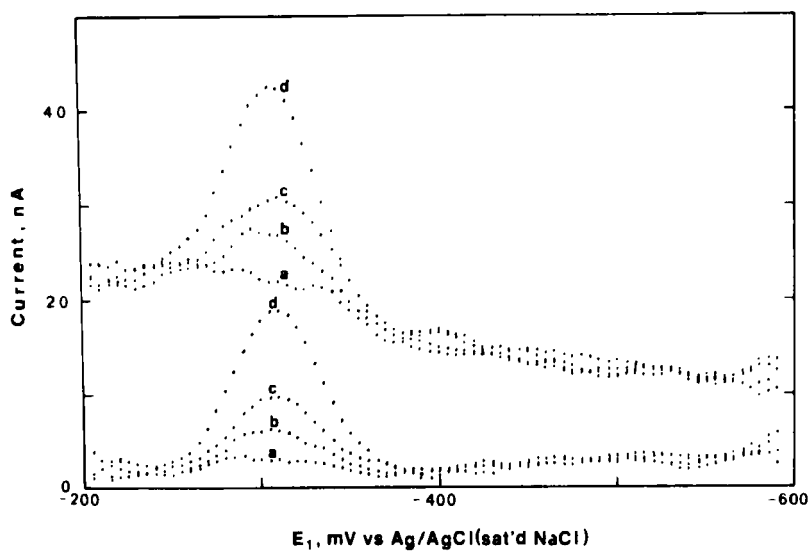


Figure 9. Alternate drop (lower curves) and ordinary (upper curves) differential pulse polarograms for Pb(II) in 0.1 F KCl (pH 2). $\Delta E = -50$ mV ; $\delta = 16.7$ msec ; $\tau = 1.0$ sec. a) 0, b) 40, c) 80, d) 160 ng Pb/ml.

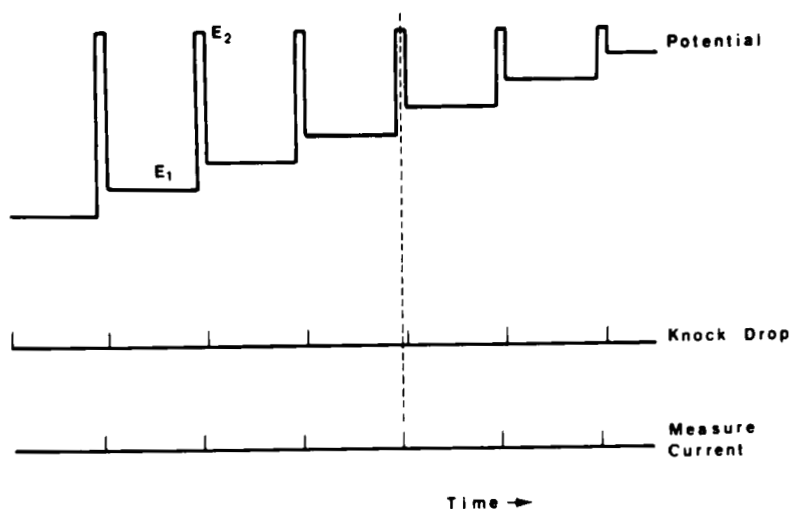


Figure 10. Schematic wave-form and timing for constant potential pulse polarography.

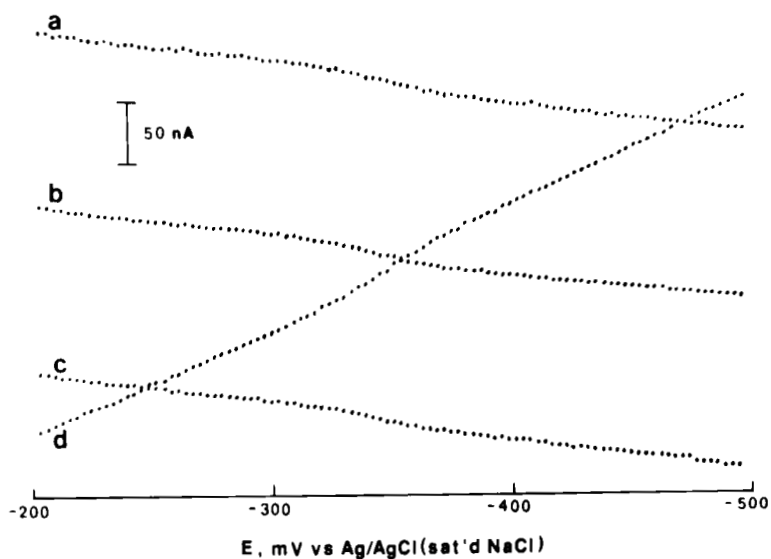


Figure 11. Constant potential pulse polarograms for 100 ng Pb/ml in 1 F HCl. $\delta = 16.7$ msec ; $\tau = 0.5$ sec. a) $E_2 = -500$ mV ; b) $E_2 = -350$ mV ; c) $E_2 = -200$ mV. Curve d is an ordinary normal pulse polarogram under the same conditions.

In this paper, we have attempted to give an overview of some of our recent work in the applications of pulse techniques in electroanalytical chemistry.

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